

[SPECIFICATION]

[Name of Invention]

Production Method For Ultra-High-Purity Ruthenium(Ru) Powder And Target By Using Waste Ruthenium(Ru) Targets

[Technological Field]

Recently, a large capacity and a high integrity related to a magnetic recording medium or next-generation memory are required very eagerly. The present invention is related to a method for manufacturing Ru powder and a target which are frequently used in a seed layer for forming a magnetic layer. In particular, the object of the present invention is to remove simply surface pollutants and foreign substances from a surface of used a waste Ru target by using a chemical method or a mechanical method, to produce ultra high purity Ru powder through plasma, pulverization and a heat process, and to produce Ru target of high density through a hot compacting process.

[Background of Invention]

The present invention is related to a method for producing evaporized or dispersed Ru powder by using heat plasma on a waste Ru target, for producing finely processed and highly purified Ru powder through a complete pulverization and a heat process, and for producing a Ru target of high density via a hot compacting. To be more specific, the present invention is related to a method for manufacturing Ru powder and a target by using environment-friendly plasma wherein the processes thereof are reduced and the manufacturing time is shortened, as compared with a manufacturing processes of Ru powder and a target employing a wet method which is essentially used in producing Ru powder.

Generally, in connection with a next-generation semiconductor memory(RAM, MRAM, FeRAM), a head(MR, TMR) and a capacitor, as a large capacity of a wafer or a hard disk is required more and more, a vertical magnetic type is applied. Thus, a Ru thin film is frequently employed in order to form a seed layer for effectively arranging a magnetic layer.

Further, since Ru powder is very expensive for manufacturing a Ru sputtering target for a thin film molding, Ru powder and a target are produced by recycling waster Ru target. In a case of a Ru target, it is difficult to process it at a normal temperature because of material properties and the Ru target has been manufactured by a sintering method instead of a dissolution method due to oxidation and volatile properties in the atmosphere at a high

temperature. Further, it is indispensable to manufacture finely processed Ru powder and powder of high purity for controlling fine crystal particles. Most of Ru powder has been manufactured by a wet method. In short, a wet dissolution using strong acid solution on a waste target is applied to a waste target. Then, a final Ru powder is manufactured through distillation, condensation, a dry process, oxidation and a heat process.

But, when a wet method is applied, there is a risk in handling due to a strong acid solution and it requires much time for acquiring a final powder and dissolution of an acid solution. Further, there are many problems that much manufacturing time and expensive cost are required because of complicated processes, and high cost is generated in handling tremendous amount of waste solution after use.

Recently, in order to compensate the shortcomings of the wet method, a manufacturing method of Ru powder using only a pulverization process was attempted, but powder was produced via only mechanical pulverization. Further, a rough pulverization of a target is performed even at the initial phase of a process and pollution is generated in a pulverization equipments due to pulverization applied for acquiring refined powder. Thus, a process using an acid solution in order to remove the pollutants is suggested, but there are many problems in a powder production of high purity.

[Contents of Invention]

[Technological Objects]

The present invention is related to a method for manufacturing refined ultra high purity Ru powder by using waste Ru target, and for manufacturing a target of high density. For realizing this method, the object of the present invention is to employ eco-friendly plasma process, to produce powder, to realize powder of high purity through refined pulverization of powder and a heat process, and to produce Ru target through a heat compaction instead of dissolution and production of powder using conventional chemical products. When a powder target is produced through this method, the production time is reduced as compared with the conventional method. Further, a waste solution is not generated since an acid solution is not used and thus the present invention is eco-friendly, the production process is simple. As a result, there is a merit that powder and a target can be produced within a very short time.

In order to realize these tasks, the object of the present invention is to remove pollutants remaining on a surface of a waste Ru target by applying a chemical method or a mechanical

method such as grinding and the like on a surface of a waste Ru target, to produce High purity Ru powder by using a plasma device, and to finally produce refined High purity Ru powder by performing refined pulverization and allocation on the produced powder.

[Technological Solution]

The present invention is characterized in that it removes pollutants and foreign substances remaining on a surface of a waste Ru target by applying a chemical method or a mechanical method on a surface of a waste Ru target, and produces Ru powder by using a plasma device, and finally produces high purity Ru powder by pulverization and a heat process. Further, the present invention is characterized in that Ru target of high purity is acquired by applying a pressure molding of a high temperature to the finally acquired High purity Ru 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, in case of the dry method which is recently published, pollution is generated due to rough pulverization and thus, a wet process is applied sometimes in order to solve the pollution problem.

But, the present invention is characterized in that it employs a dry method instead of a wet method in producing Ru powder and produces Ru powder by using plasma instead of rough pulverization. Through such manufacturing method, L/T of a final powder and a target is shortened. In addition, a refined Ru powder and target of high purity can be realized. Thus, functional improvement of a sputtering target material is expected.

[Brief Description of Drawings]

FIG. 1 is a diagram illustrating FESEM image of an evaporated Ru powder produced by applying plasma to a waste Ru target.

FIG. 2 is a diagram illustrating FESEM image of a dispersed Ru powder produced by applying plasma to a waste Ru target.

FIG. 3 is a diagram illustrating FESEM image of Ru powder undergoing through

pulverization, an atmospheric process and a hydrogen heat process by using Ru powder produced by plasma.

[Best Mode for realizing Invention]

When producing Ru powder and a target of ultra high purity by using a waste Ru target, the present invention provides a method for manufacturing Ru powder and a target of ultra high purity by using waste Ru, which is characterized in that it includes a step for removing surface pollutants and foreign substances remaining on a surface of a waste Ru target by using a chemical method or a mechanical method; a step for producing Ru powder on waste Ru wherein surface pollutants and foreign substances are removed by using plasma; a step for producing high purity Ru powder on the produced Ru powder through a heat process and pulverization process; a step for Ru powder sinter of high density by applying a pressure molding of high temperature to high purity Ru powder; a step for producing Ru target wherein a surface roughness is controlled via a post-processing.

[Embodiments of Invention]

When producing Ru powder by using a waste Ru target, the present invention is characterized in that plasma is used instead of a conventional wet method or any mechanical methods for producing powder. Further, the present invention is characterized in that a final refined high purity Ru powder is produced through refined pulverization of powder and a heat process. The production time is reduced remarkably through this production process, and it is possible to produce Ru powder by using an eco-friendly process since use of an acid solution is suppressed for dissolution or removing pollutants, as compared with the conventional wet method. Further, it is possible to produce Ru target of high purity having refined crystal particles by applying a pressure molding of a high temperature to the produced High purity Ru powder.

The present invention is related to a method for manufacturing Ru powder and a target of ultra high purity by using a waste Ru target. Further, it is characterized by a step for removing surface pollutants and foreign substances remaining on a surface of a waste Ru target by using a chemical method or a mechanical method; a step for producing Ru powder on waste Ru target wherein surface pollutants and foreign substances are removed by using plasma; a step for producing high purity Ru powder on the produced Ru powder through a heat process and pulverization process; a step for Ru powder sinter of high density by

applying a pressure molding of high temperature to high purity Ru powder ; a step for producing Ru target wherein a surface roughness is controlled via a post-processing.

Below, the above steps are explained in detail.

First of all, surface pollutants and foreign substances remaining on a surface of a waste Ru target are removed by using a chemical method or a mechanical method.

There is a high possibility that in connection with a surface of a waste Ru target, a surface contamination due to handling, or contamination due to a Back Depo during a sputtering process may be generated and contamination can also be generated due to foreign substances formed through exposure to the atmosphere for a long time. When producing powder by using these contaminated waste targets, the remaining pollutants or foreign substances are introduced into the powder and thereby, the introduction reduces a degree of purity of powder or a degree of purity of a final target. Therefore, it is a must to remove the pollutants or foreign substances before the production processes of powder. In order to remove the pollutants, it is possible to employ a chemical method including the steps for depositing the pollutants into a Ru solvent for a short time and for cutting the surface thereof by several tens of μm , or it is possible to remove a thickness layer by a predetermined level by using a processing device such as a lathe or a grinder. When a removing step is performed by the above mechanical processing methods, it is possible to remove a thickness of about 0.1mm. 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.

Next, a Ru powder is produced by applying heat plasma to a waste Ru target wherein pollutants and foreign material are removed.

As for the production procedures of powder, an interior side of a chamber of plasma in order to produce powder of high purity is washed and a waste target is set on a crucible, and then, plasma is formed and thereby, powder is acquired.

First of all, it is possible to wash inside of a chamber before a plasma treatment so that foreign material can not be mixed or introduced. Further, it is necessary minimize contamination due to an electrode used in forming a heat plasma or a mold in order to manufacture powder of high purity. Thus, graphite, copper(Cu), molybdenum(Mo), tungsten(W) or ruthenium(Ru) can be used as the substances of mold. In order to prevent contamination due to mold, it is most possible to use Ru mold of the same material. In case of Ru having very high brittleness, it is difficult to produce it because of the difficult

processes thereof. Therefore, it is possible to use a carbon mold which can be easily removed even if contamination is generated. As an electrode material which can be used in a plasma treatment, molybdenum(Mo), tungsten(W) or ruthenium (Ru) can be employed, but it is most possible to employ Ru of the same material so as to minimize pollution due to electrodes.

For forming plasma, a vacuum pump is used and decompression is executed. Then, electricity is applied after adjusting injection level of reaction gas and a working vacuum level. As the reaction gases for forming plasma, Ar, H₂, N₂, CH₄, Ar+H₂, and Ar+N₂ can be used. Further, there is a high possibility that H₂, N₂, O₂ remain in a final Ru powder. Thus, H₂, N₂, O₂ are not eliminated completely by an atmospheric process and a hydrogen heat process and they may remain. Therefore, when using a target, particles or arc are generated by the remaining gases during a film forming process and thereby, yield is reduced or the properties of a semiconductor product are affected. As a result, it is most beneficial to employ Ar. However, even if it is possible to use H₂ and N₂ or the gas component remains in the produced powder due to remaining O₂ in a chamber in order to increase a powder manufacturing speed for securing productivity, when it is possible to remove the remaining gas completely through a degassing process after processing the powder minutely, it is also possible to use H₂, N₂, O₂.

After forming plasma, Ru powder is produced by increasing electricity. If electricity provided to plasma is increased, a molten metal is formed, and the temperature of the metal is increased. The metal exceeding an evaporation temperature is evaporated and cooled so that powder can be produced or the metal is dispersed due to a surrounding atmosphere and a pressure of a reaction gas and thereby, powder is produced. At this time, it is most suitable that the applied electricity ranges from 10 to 100kw. If the electricity is less than 10kw, there is a possibility that forming of a molten metal, evaporation or dispersing may not be generated easily. Taking security of equipments into consideration, the concerned processes are performed at below 100kw.

Next, Ru powder of a high purity is produced by applying a heat process and a pulverization process to the produced Ru powder. In case of Ru powder produced by using plasma, the evaporated powder exhibits very fine size of hundreds of nm level. But, in a case that it is dispersed, coarse powder of several tens of μm are acquired. A target having uniform and fine crystal particles is very advantageous so as to obtain Ru thin film of high quality which is manufactured as a target. Thus, it is advantageous that a particle size of powder for

manufacturing a target is refined and uniform. But, when only refined powder is used for powder produced by plasma, entire yield is reduced remarkably. Thus, the present invention is characterized in that refined and highly purified powder can be produced by allowing all of coarse powder to be used.

Ball Mill, Planetary Mill or Jet Mill which is generally used in a refined pulverization is available as a pulverizing method to increase yield of powder produced by plasma. At this time, Jet Mill is frequently used. The main reason of it is that pulverization can be easily performed in Ru, but pollution can be generated due to the ball when large amount of quantity must be processed or a working hour may be increased. Thus, a pulverizing process using Jet Mill without using a ball is terribly advantageous in acquiring Ru of high purity.

Further, there is possibility that a carbon component may remain in the pulverized powder due to a reaction gas or use of a widely-used carbon crucible. It is possible to produce high purity Ru powder through the hydrogen heat process after the atmospheric heat process.

For example, a carbon, a mold material is contaminated by several wt% in producing powder by using high plasma heat and thus, it is possible to remove the contaminated carbon since the carbon is vaporized into CO or CO₂ through a simple atmospheric heat process. Ru is oxidized by the atmospheric heat process for removing carbons to acquire a blue oxide substance of Ru. Subsequently, it is possible to produce High purity Ru powder through a hydrogen heat process.

As for heat process conditions, in case of the atmospheric heat process, it is possible to perform a heat process at the temperature of 600-1000 °C for 1-5 hours. In a case that a heat process is performed at temperature below 600 °C and for less than one hour, there is a high possibility that remaining carbons may not be removed completely. In a case that a heat process is performed at temperature above 1000 °C and for more than 5 hours, there is a high possibility that the produced powder may be condensed.

In a case of a hydrogen heat process, it is possible to perform a heat process at 800-1000 °C for 1-5 hours. The main reason of it is that Ru deoxidization is not realized sufficiently at a temperature below 800 °C and for less than one hour, and there is a high possibility that powders may be condensed at a temperature above 1000 °C and for more than 5 hours. Ru sinter of high density is produced by applying a pressure molding of a high temperature to refined and high purity Ru powder acquired by a heat process. At this time, it is possible

to produce Ru sinter by using any one selected from Hot Press, Hot Isostatic Press, or Spark Plasma Sintering, which is used as a pressure molding of high temperature. Further, in order to produce Ru sinter of high purity, it is most possible to employ a hot compaction method which can easily remove the remaining oxygen in Ru powder or impure gases such as C, N and H.

In order to produce Ru sinter of high density, it is to be understood that a pressure of 10-80 MPa can be applied at a high temperature and a sintering temperature ranges from 1300 to 1700°C. If the applied pressure is below 10 MPa and the sintering temperature is below 1300°C, there is a high possibility that a sinter of low density may be produced. If the sintering temperature is above 1700°C, a sinter having coarse crystal particles is produced and thereby, there is a high possibility that a property of a sputtering target may be deteriorated. Further, it is advantageous to work at below 80MPa for protecting an expensive carbon mold which is widely used at a high sintering temperature.

A lathe process and a grinding process are performed for Ru sinter of high density produced through a pressure molding of high temperature and then, a surface roughness for sputtering is secured and a final target is produced.

In case of Ru sinter of high density produced through a pressure molding of high temperature, some carbons may be contaminated on a contact part of a used carbon mold or a carbon sheet and thereby, it may affect a thin film when a sputtering is performed. For preventing this phenomenon, it is possible to remove a thickness of 0.1-1 mm by performing a lathe process or a grinding process. The main reason of it is as follows. There is a high possibility that carbons may remain if the thickness is too thin, and the entire yield is reduced if the thickness is above 1 mm, and thereby the total cost may be increased. Further, in a case of a Ru target which is used for a semiconductor product, a surface roughness affect upon properties of a thin film and thus, it is possible to maintain the surface roughness below 1 μ m. A step for maintaining the surface roughness can be realized through a grinding process. It is also possible to remove the remaining thickness through a grinding process after removing a predetermined thickness through a lathe process in order to shorten a whole manufacturing period.

[Embodiment]

1.8kg of a waste Ru target having 3N7 purity, and a crystal particle of 14 μ m, which is used as a seed layer of a hard disk, is purchased to produce Ru powder using a waste Ru target.

The waste Ru target was deposited in NaClO for 30 minutes to eliminate foreign substances or pollutants on a surface of a waste Ru target and the solution existing on the surface was washed. In connection with the waste Ru target in which foreign substances are removed, 1.8kg of Ru powder was produced by using a heat plasma device.

Ru powder produced by plasma is illustrated in FIG. 1 and 2.

FIG. 1 illustrates evaporated Ru powder having a spherical shape of several nm and FIG. 2 illustrates dispersed Ru powder having a spherical shape of 100 μ m. For the produced Ru powder, pulverization was performed by using Jet Mill and for the pulverized Ru powder, a heat treatment was performed at 800 $^{\circ}$ C for one hour under atmosphere. Therefore, the remaining carbon was removed. Then, a hydrogen heat process was performed at 800 $^{\circ}$ C for 30 minutes and deoxidization was performed for Ru powder oxidized during an atmospheric heat process. Thus, a final highly purified and minutely refined powder was acquired. Pulverization and the shape of the final powder processed by heat are illustrated in FIG. 3.

The pulverized Ru powder has a shape of a fragment, and as a result of analyzing a particle size, it turns out that it consists of very refined powder having a center particle size of 4 μ m.

In order to confirm the ratio of impure substances in a waste target and Ru dry powder produced by using the waste target, analysis of impurities(embodiment 1) was performed through GDMS(Glow Discharge Mass Spectrometry) analysis. Further, in order to understand the state of produced Ru powder, High purity Ru powder which is being sold in the market was procured and then, analysis was realized via GDMS. The results(comparison example 1)are illustrated in table 1. It is to be understood from table 1 that in case of Ru powder acquired according to the present invention, Ru powder maintains the same level as that of the waste target in terms of the content of impurities and degree of purity except oxygen, and in case of commercially used Ru powder, Na and Cl were not removed completely because of use of an acid solution. Thus, it is to be understood that the impure content exceeded 200 ppm and the degree of purity was low.

[table 1]

(unit : ppm)

Impurities	a waste target	embodiment 1	comparison example 1
Fe	20	23	21

Si	2	12	36
Cl	14	-	32
Na	3	2	25
K	28	<1	25
Ca	10	5	6
Mg	5	8	11
Pd	18	15	-
W	3	10	-
Pt	25	20	28
Rh	<1	10	25
U	-	-	-
Th	-	-	-
O	120	680	890
Total of impurities(O is excluded)	128	105	209
Final degree of purity	3N8	3N8	3N7

A sintering test was performed by using a high temperature press for dry powder of Ru obtained according to the present invention, and a purchased Ru powder. Then, the properties of produced sinters were compared(embodiment 2, comparison example 2). Further, in order to compare physical properties of the produced sinters, the properties of a waste Ru target purchased for production of powder were compared(comparison example 3).

[table 2]

Items	Embodiment 2	comparison example 2	comparison example 3
Density(gr/cm ³)	12.34	12.32	12.33
Relative Density(%)	99↑	99↑	99↑
Degree of purity	99.98↑	99.97↑	99.98↑
A particle size(μm)	6	15	18

As from the table 2, when Ru sinter produced according to the present invention was compared with the sinter produced by using Ru powder which may be produced through a wet method, both exhibit more than the same levels in terms of density and a degree of purity. Further, as a result of comparing the commercially used Ru target and the present invention, it turned out that there are no remarkable differences. In particular, in terms of the size of a crystal particle, it turned out that Ru sinter of the present invention exhibits refined crystal particles as compared with the sinter produced by a conventional wet method or a conventional waste Ru target.

[Industrial Applicability]

According to the present invention, a dry method is used instead of a wet method for producing Ru powder and the present invention is characterized in that Ru powder is produced by using plasma instead of rough pulverization. Through such manufacturing method, L/T of a final powder and a target is shortened. In addition, a refined Ru powder and target of high purity can be realized. Thus, functional improvement of a sputtering target material is expected.

[Claims]

1. A method for manufacturing ultra high purity Ru powder and target by using waste Ru comprising,

(a) a step for removing surface pollutants and foreign substances remaining on a surface of a waste Ru target by using a chemical method or a mechanical method;

(b) a step for producing Ru powder on waste Ru wherein surface pollutants and foreign substances are removed by using plasma;

(c) a step for producing high purity Ru powder on the produced Ru powder through a heat process and pulverization process;

(d) a step for Ru powder sinter of high density by applying a pressure molding of high temperature to high purity Ru powder;

(e) a step for producing Ru target wherein a surface roughness is controlled via a post-processing.

2. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 1, wherein the chemical method or the mechanical method is employed in order to remove surface pollutants and foreign substances remaining on a surface of a waste Ru target.

3. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 2, wherein NaClO solution or solution including NaClO is employed as the chemical method to remove surface pollutants and foreign substances remaining on a surface of a waste Ru target.

4. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 2, wherein a lathe and a grinding processing is employed as the mechanical method to remove surface pollutants and foreign substances remaining on a surface of a waste Ru target.

5. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 1, wherein a material of a mold in the step for producing Ru powder by using plasma is any one selected from graphite, copper(Cu), molybdenum(Mo), tungsten(W) or Ruthenium(Ru).

6. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 1, wherein a material of an electrode in the step for producing Ru powder by using plasma is any one selected from molybdenum(Mo), tungsten(W) or Ruthenium(Ru).
7. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 1, wherein one or more gases selected from Ar, H₂, N₂, or CH₄ are employed when producing the plasma.
8. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 1, wherein an atmospheric heat process or a hydrogen heat process is employed as a heat process of Ru powder manufactured by using the plasma so that high purity Ru powder can be obtained.
9. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 8, wherein the atmospheric heat process is performed under 800-1000 °C for 1-5 hours.
10. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 8, wherein the hydrogen heat process is performed under 800-1000 °C for 1-5 hours.
11. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 1, wherein pulverizing Ru powder manufactured by using the plasma is performed by any one selected from Ball Mill, Planetary Mill or Jet Mill.
12. The method for manufacturing ultra high purity Ru powder and target by using waste Ru according to the claim 1, wherein the high temperature pressure molding is performed by any one selected from Hot Press, Hot Isostatic Press, or Spark Plasma Sintering.