

DESCRIPTION

Title of Invention: SPUTTERING TARGET AND PRODUCTION METHOD THEREFOR

Technical Field

[0001]

The present invention relates to a sputtering target and a production method therefor.

Background Art

[0002]

Target materials made by sintering MoSi_2 powder by hot pressing (referred to hereinafter also as “HP”) have been used for Mo-Si-based sputtering targets used for mask blanks etc. In producing such MoSi_2 target materials sintered by HP, sintering at high temperatures is necessary. This tends to increase the Si crystal grain size after sintering. An increase in the Si crystal grain size is a cause of increase in the creation of particles at the time of sputtering.

[0003]

With the aim of suppressing the creation of particles at the time of sputtering, Patent Literature 1 proposes a silicide target for sputtering having a density of 99% or greater, and in which the amount of presence of a large silicon phase appearing on the sputtering surface and having a size of 10 μm or greater is 1 grain/ mm^2 or less and the oxygen content is 150 ppm or less. Patent Literature 2 discloses a sputtering target including from 70 to 97 wt% of silicon, with the remainder consisting substantially of a high-melting-point metal silicide. The metallographic structure of the target includes at least a silicon phase and a high-melting-point metal silicide phase made of silicon and a high-melting-point metal, and on the sputtering surface, the half-width of the peak of the Si (111) plane found by X-ray diffraction analysis is 0.5 degrees or less and the half-width of the peak of the high-melting-point metal silicide (101) plane is 0.5 degrees or less.

[0004]

Patent Literature 3 discloses a sputtering target for forming a light semi-transmissive film on a light-transmissive substrate. The target is made substantially of a metal and silicon, wherein silicon is included in an amount that is greater than the stoichiometrically stable composition between the metal and silicon, and thus silicon is present as metal silicide grains and silicon grains. Further, the average grain size and/or the grain size distribution of the metal silicide grains are/is set such that the defect occurrence rate in the light semi-transmissive film becomes less than or equal to a predetermined value.

[0005]

Patent Literature 4 discloses a sputtering target that includes a metal silicide and silicon and is used at the time of producing a mask blank by sputtering. The Literature describes that, with this target, the creation of particles can be reduced.

Citation List

Patent Literature

[0006]

Patent Literature 1: US Patent No. 5,460,793

Patent Literature 2: JP 2002-173765A

Patent Literature 3: JP 2005-200688A

Patent Literature 4: JP 2004-109317A

Summary of Invention

[0007]

As described above, various attempts have been made to reduce the number of particles created at the time of sputtering using a Mo-Si-based sputtering target. However, given the current circumstances in which particle characteristics demanded of mask blanks are becoming increasingly stricter, there has yet to be provided a sputtering target capable of reducing the creation of particles to a satisfiable level.

[0008]

An objective of the present invention is to provide an improved sputtering target, and more specifically, a sputtering target in which the creation of particles at the time of sputtering is suppressed compared to conventional art, and a method for producing the sputtering target.

[0009]

The present invention provides a sputtering target having a molybdenum content of from 3 to 25 mol% and a silicon content of from 75 to 97 mol%, wherein: the sputtering target includes a silicon phase in which an average grain size of silicon grains is 2.0 μm or less, and a molybdenum silicide phase in which an average grain size of molybdenum silicide grains is 2.5 μm or less; and an average number of holes present in the silicon phase and having a major axis of 0.3 μm or greater is ten or fewer within an area of 90 $\times$ 125 μm .

[0010]

The present invention also provides, as a suitable method for producing the aforementioned sputtering target, a production method for producing a sputtering target, the method involving steps of: mixing a molybdenum powder and a silicon powder; subjecting the obtained powder mixture to a spark plasma sintering process; and then subjecting the powder mixture to a hot isostatic pressing process, wherein, in the step of subjecting the powder mixture to the hot isostatic pressing process, the sintering temperature is from 1150°C to 1350°C.

Brief Description of Drawings

[0011]

[Fig. 1] Fig. 1 is a schematic diagram illustrating a position for measuring the major axis of a hole formed in a sputtering target.

Description of Embodiments

[0012]

The present invention is described below according to preferred embodiments thereof. A sputtering target of the present invention includes silicon and molybdenum.

More specifically, the sputtering target of the present invention preferably has a molybdenum content of from 3 to 25 mol%, more preferably from 3.3 to 24 mol%, even more preferably from 3.5 to 23 mol%. The silicon content is preferably from 75 to 97 mol%, more preferably from 76 to 96.7 mol%, even more preferably from 77 to 96.5 mol%. Further, the sputtering target of the present invention includes a phase constituted by silicon (referred to hereinafter also as “silicon phase”) and a phase constituted by molybdenum silicide (referred to hereinafter also as “molybdenum silicide phase”). The sputtering target having such a structure is a so-called silicon-rich target, wherein, for example, the composition of the target includes a greater amount of silicon than a stoichiometrically stable composition. By including silicon in an amount that is greater than the stoichiometrically stable composition between molybdenum and silicon (i.e., by making the composition silicon-rich), silicon is present as molybdenum silicide grains and silicon grains.

[0013]

The molybdenum content and the silicon content in the sputtering target of the present invention can be considered identical to the mixture ratio (in mol%) between molybdenum powder and silicon powder employed as materials, but can also be found, for example, by methods such as inductively coupled plasma optical emission spectrometry (ICP) with an ICP analysis device by employing, as a measurement target, a liquid obtained by dissolving the sputtering target.

[0014]

The sputtering target of the present invention is preferably made of elemental silicon and molybdenum silicide, but may include small amounts of elemental molybdenum, a solid solution of silicon and molybdenum, or other metal elements, so long as those components do not negatively affect the advantageous effects of the present invention. The content of components other than elemental silicon and molybdenum silicide is preferably 1.0 mass% or less with respect to the mass of the sputtering target.

[0015]

A feature of the present invention involves controlling the average grain size of

silicon grains of the sputtering target to be within a specific range, and controlling the average grain size of molybdenum silicide grains to be within a specific range. More specifically, Inventors' study results have revealed that, by controlling the average grain size of silicon grains to be preferably 2.0 μm or less, the creation of particles caused by arcing at the time of sputtering can be suppressed effectively. From this viewpoint, the average grain size of silicon grains is more preferably 1.9 μm or less, even more preferably 1.8 μm or less, further more preferably 1.7 μm or less. The lower limit value of the average grain size of silicon grains is not particularly determined, but is typically 0.1 μm or greater.

[0016]

On the other hand, Inventors' study results have revealed that, by also controlling the average grain size of molybdenum silicide grains to be preferably 2.5 μm or less, the creation of particles caused by arcing at the time of sputtering can be suppressed effectively. From this viewpoint, the average grain size of molybdenum silicide grains is more preferably 2.2 μm or less, even more preferably 2.1 μm or less, further more preferably 2.0 μm or less. The lower limit value of the average grain size of molybdenum silicide grains is not particularly determined, but is typically 0.1 μm or greater.

[0017]

The average grain size of silicon grains and the average grain size of molybdenum silicide grains can be measured according to the following method.

Method for Measuring Average Grain Size:

First, the surface of a sputtering target material is polished and smoothed. On the smoothed surface, the energy dispersive X-ray spectrometry (EDS) spectrum and electron backscatter diffraction (EBSD) pattern of silicon and molybdenum silicide are measured with a FE-gun type scanning electron microscope (SUPRA 55VP from Carl Zeiss) provided with an EDS/EBSD device (Pegasus System from AMETEK, Inc.). The measurement conditions are as follows: accelerating voltage: 20 kV; magnification: 3000x; field of view: 10 $\times$ 20 μm ; measurement interval: 0.02 μm . The crystal phases to be indexed are the silicon phase and the molybdenum silicide phase, and the two are

distinguished from the EDS spectrum. Respective area-weighted average crystal grain sizes (μm) of the silicon phase and the molybdenum silicide phase are calculated for the obtained data by selecting the analysis menu “Grain Size” in an EBSD analysis program (OIM Analysis from TSL Solutions). Misorientations of 5° or greater are identified as general boundaries, whereas twin boundaries in an orientation relationship of 70° of rotation about the $\langle 001 \rangle$ axis are not considered general boundaries. This measurement is performed randomly in five fields of view, and the respective average crystal grain sizes of the silicon phase and the molybdenum silicide phase in each field of view are calculated. The average crystal grain sizes of the silicon phases and molybdenum silicide phases obtained in the respective fields of view are further averaged, and the respective average values are considered the average crystal grain size of the silicon phase and that of the molybdenum silicide phase of the sputtering target.

[0018]

In addition to the feature that the average grain size of silicon grains in the silicon phase is equal to or below the aforementioned value, the sputtering target of the present invention has another feature that the average number of holes present in the silicon phase and having a major axis of $0.3 \mu\text{m}$ or greater is ten or fewer within a rectangular area of $90 \times 125 \mu\text{m}$. “Holes” present in the silicon phase can also be referred to as “voids” or “defects”, and are, in other words, spaces in the silicon phase where no substance is present. Inventors’ study results have revealed that, when holes are present in the silicon phase, the holes are likely to act as points of origination where particles are created due to arcing at the time of sputtering, and by reducing the size of the holes as well as the number of holes present, the creation of particles can be suppressed effectively. The holes can be reduced by making the silicon grains in the silicon phase grow sufficiently. However, if the average grain size of the silicon grains becomes too large, this may also make it likely to create particles due to arcing at the time of sputtering, as described above. Thus, in the present invention, a balance is achieved between the average grain size of silicon grains in the silicon phase and the size of the holes, to thereby effectively suppress the creation of particles at the time of sputtering.

[0019]

From the viewpoint of further enhancing the aforementioned effects, it is preferable that the average number of holes present in the silicon phase and having a major axis of 0.3 μm or greater is preferably five or fewer, more preferably three or fewer, in a rectangular field of view of $90 \times 125 \mu\text{m}$ as observed under a scanning electron microscope.

[0020]

The major axis of a hole in the silicon phase and the average number of holes can be measured according to the following method.

Method for Measuring Average Number of Holes Having Major Axis of 0.3 μm or Greater:

First, the surface of a sputtering target is polished and smoothed. The smoothed surface is magnified with a scanning electron microscope (JXA-8800-R from JEOL Ltd.) to a magnification of 1000x, to obtain a rectangular field of view of $90 \times 125 \mu\text{m}$. Further, the surface is magnified to 5000x, and the number of holes having a major axis of 0.3 μm or greater within the aforementioned field of view is counted. This measurement is performed randomly in 10 fields of view, and the numbers of holes in the respective fields of view are averaged, and the average value is considered the average number of holes having a major axis of 0.3 μm or greater in that sputtering target. The major axis of each hole is the length in the longest direction of the hole that is present (see Fig. 1).

[0021]

In order to control the average grain size of silicon grains and the average grain size of molybdenum silicide grains to be within the aforementioned ranges and to also control the major axis of each hole in the silicon phase to be within the aforementioned range, it is advantageous, for example, to produce the target of the present invention by employing, in combination, the later-described spark plasma sintering process (abbreviated hereinafter also as “SPS process”) and hot isostatic pressing process (abbreviated hereinafter also as “HIP process”).

[0022]

The sputtering target of the present invention has a relative density of 99% or

greater, preferably 99.5% or greater, more preferably 99.7% or greater, even more preferably 100% or greater, further more preferably 100.5% or greater. Increasing the relative density of the target reduces the pores (holes) in the target; thus, electric discharge at the time of sputtering becomes stable, and thereby the creation of particles due to arcing can be prevented. The higher the relative density, the more preferable, and the upper limit value is not particularly determined, but is typically 102%. Relative density is measured according to the Archimedes' method. More specifically, the mass in air of the sputtering target is divided by its volume (which is the mass in water of the sputtering target, divided by the specific gravity of water at the measurement temperature), and the percentage value of the quotient to the theoretical density ρ (g/cm^3) is found as the relative density (unit: %).

[0023]

The sputtering target of the present invention is constituted substantially by silicon and molybdenum silicide (MoSi_2). Thus, the theoretical density ρ can be calculated from the following equation (1).

$$\rho = \{(C_1/100)/\rho_1 + (C_2/100)/\rho_2\}^{-1} \dots (1).$$

Density of silicon: $\rho_1=2.33 \text{ g/cm}^3$;

Mass percentage (mass%) of silicon: C_1 ;

Density of molybdenum silicide (MoSi_2): $\rho_2=6.24 \text{ g/cm}^3$;

Mass percentage (mass%) of molybdenum silicide (MoSi_2): C_2 .

[0024]

C_1 and C_2 above can be calculated from analytic values found by analyzing the mass percentage of silicon and the mass percentage of molybdenum in the sputtering target of the present invention by, for example, ICP optical emission spectrometry. Note that the relative density of the sputtering target of the present invention may exceed 100%, because it is expressed as a percentage value to the theoretical density ρ (g/cm^3). Further, since the amounts elemental molybdenum, solid solutions of silicon and molybdenum, and other elements are very small, these can be ignored when calculating the theoretical

density.

[0025]

In the sputtering target of the present invention, the number of aggregates created by aggregation of the molybdenum silicide grains and having a circle-equivalent diameter of 10 μm or greater (referred to hereinafter also as “molybdenum silicide grain aggregates”) is preferably $1/\text{mm}^2$ or fewer. By controlling the number of molybdenum silicide grain aggregates to be $1/\text{mm}^2$ or fewer, the occurrence of arcing originating from the sections of the aggregates can be suppressed, and thus, it is possible to obtain a sputtering target in which the creation of particles due to arcing is reduced. From this viewpoint, it is preferable that the number of molybdenum silicide grain aggregates is more preferably $0.8/\text{mm}^2$ or fewer, even more preferably $0.5/\text{mm}^2$ or fewer, further more preferably $0.2/\text{mm}^2$ or fewer. The closer the number of molybdenum silicide grain aggregates is to zero, the more preferable.

[0026]

The number of molybdenum silicide grain aggregates can be measured as follows.

Method for Measuring Aggregates:

First, the surface of a sputtering target is polished and smoothed. The smoothed surface is magnified with a scanning electron microscope (JXA-8800-R from JEOL Ltd.) to a magnification of 200x, and images of 30 fields of view, each being a 0.5×0.65 mm rectangle, are captured randomly. From each obtained image, the number of aggregates created by aggregation of the molybdenum silicide grains and having a circle-equivalent diameter of 10 μm or greater is counted by using grain analyzing software (Grain Analysis (Version 3.0) from Sumitomo Metal Technology Inc.). The obtained numbers of the molybdenum silicide grain aggregates are summed up, the total is divided by 9.75 mm^2 (i.e., thirty 0.5×0.65 -mm fields of view), and the quotient is found as the number of molybdenum silicide grain aggregates per 1 mm^2 .

[0027]

Next, a suitable method for producing the sputtering target of the present invention is described. The sputtering target of the present invention is suitably produced through

steps of mixing a molybdenum powder and a silicon powder, and subjecting the obtained powder mixture to a spark plasma sintering process.

[0028]

To obtain the target of the present invention, first, an elemental molybdenum powder and an elemental silicon powder are prepared, and the powders are mixed. From the viewpoint of providing the molybdenum silicide phase with a fine structure, it is preferable to use, for the molybdenum powder, a powder in which the specific surface area as measured by the Brunauer-Emmett-Teller (BET) method is $4.0 \text{ m}^2/\text{g}$ or greater. From the viewpoint of further enhancing this advantage, it is preferable that the specific surface area of the molybdenum powder is preferably $5.0 \text{ m}^2/\text{g}$ or greater, more preferably $6.0 \text{ m}^2/\text{g}$ or greater. The upper limit value of the specific surface area of the molybdenum powder is not particularly determined, but is preferably $8.0 \text{ m}^2/\text{g}$ or less from the viewpoint of preventing aggregation of the molybdenum powder.

[0029]

On the other hand, it is preferable to use, for the silicon powder, a powder in which the specific surface area as measured by the BET method is $4.0 \text{ m}^2/\text{g}$ or greater, from the viewpoint of providing the silicon phase and the molybdenum silicide phase with fine structures. From the viewpoint of further enhancing this advantage, it is preferable that the specific surface area of the silicon powder is preferably $5.0 \text{ m}^2/\text{g}$ or greater, more preferably $6.0 \text{ m}^2/\text{g}$ or greater. The upper limit value of the specific surface area of the silicon powder is not particularly determined, but is preferably $8.0 \text{ m}^2/\text{g}$ or less from the viewpoint of preventing aggregation of the silicon powder.

[0030]

The respective specific surface areas of the molybdenum powder and the silicon powder can be measured according to the single-point BET method with, for example, an automatic surface area measurement device (Macisorb (registered trademark) HM model-1210 from Mountech Co. Ltd.) by employing a mixed gas (30 vol% nitrogen and 70 vol% helium) as the adsorption gas. The shapes of the molybdenum powder and the silicon powder are not particularly limited, so long as their specific surface areas are

within the aforementioned ranges.

[0031]

The mixing ratio, in mol%, of the molybdenum powder and the silicon powder expressed as the value $\text{Mo}/(\text{Mo}+\text{Si})\times 100$ is preferably from 3 to 25%, more preferably from 3.3 to 24%, even more preferably from 3.5 to 23%. Further, the value $\text{Si}/(\text{Mo}+\text{Si})\times 100$ is preferably from 75 to 97%, more preferably from 76 to 96.7%, even more preferably from 77 to 96.5%. By mixing molybdenum and silicon at this ratio, the intended target can be obtained successfully.

[0032]

Various mixing means can be used for mixing the molybdenum powder and the silicon powder. For example, it is possible to use a medium agitation-type mill, such as a bead mill, a sand mill, an Attritor (registered trademark) or a ball mill, or a three roll mill. When using a medium agitation-type mill, it is preferable that the diameter of the medium is from 5 to 20 mm. Preferably, the material of the medium is, for example, zirconia or alumina. Further, the obtained powder mixture may be sifted with a sieve having a mesh opening of 50 μm or less. Further, the sifted powder mixture may be pre-sintered with the aim of adjusting the specific surface area.

[0033]

The powder mixture is then charged into a sintering die having a molding depression with a predetermined shape. For example, a graphite-made sintering die may be used, but the material is not limited thereto. After charging the powder mixture into the sintering die, the powder mixture is subjected to a SPS process. The SPS process is a type of solid compression sintering process similar to a hot press sintering process (abbreviated hereinafter also as “HP process”). In the SPS process, the powder mixture charged in the sintering die is heated while being pressurized. The HP process also performs heating while pressurizing, but the way heating is performed in the SPS process is different from the HP process. In the HP process, a sintering object is heated from outside over a long period of time by using a heat-generating element of a hot press device, whereas in the SPS process, an on-off DC pulse voltage and current are applied

directly to the electroconductive sintering die and sintering object. The self-heating of the sintering die, to which electric energy has been directly introduced, is employed as the sintering drive force together with pressurization. Stated differently, in addition to thermal and mechanical energy typically used for sintering, SPS also employs, in combination as the sintering drive force, electromagnetic energy by the pulse current passage, the self-heat generation of the object being processed, and spark plasma energy produced among the grains. With the SPS process employing such a sintering method, it is possible to produce a closely packed sintered compact in which grain growth is suppressed. Stated differently, it is possible to control the average grain size of the silicon grains and the average grain size of the molybdenum silicide grains to be within the aforementioned ranges.

[0034]

From the viewpoint of obtaining the intended target successfully, the temperature rise rate when performing the SPS process is preferably from 5 to 20°C/min, more preferably from 10 to 18°C/min. By setting the temperature rise rate to 5°C/min or higher, abnormal grain growth can be suppressed. By setting the rate to 20°C/min or lower, variations in the temperature within the sintered compact can be suppressed. The sintering temperature is preferably from 1100°C to 1200°C, more preferably from 1120°C to 1200°C. By setting the sintering temperature to 1100°C or higher, it is possible to inhibit the density of the sintered compact from being reduced. By setting the temperature to 1200°C or lower, occurrence of elution can be suppressed. The sintering temperature can be found by measuring the surface temperature of the sintering die by using a radiation thermometer (IR-AHS0 from Chino Corporation). The pressure during sintering is preferably from 25 to 80 MPa, more preferably from 27 to 50 MPa. The sintering retention time is preferably from 20 to 300 minutes, more preferably from 30 to 180 minutes, on condition that the sintering temperature and the pressure are within the aforementioned ranges.

[0035]

The sintering atmosphere may be a vacuum or an inert gas. In cases of performing sintering in a vacuum, it is preferable to employ a condition that is 30 Pa or

lower, particularly 10 Pa or lower, in absolute pressure. In cases of performing sintering in an inert gas, argon or nitrogen can be used as the inert gas.

[0036]

In the present production method, it is advantageous to perform a HIP process following the SPS process. By producing a sputtering target by employing the SPS process and the HIP process in combination, it is possible to effectively suppress the creation of holes in the silicon phase while suppressing grain growth of the silicon grains and the molybdenum silicide grains.

[0037]

From the viewpoint of obtaining the intended target successfully, the temperature rise rate when performing the HIP process is preferably from 5 to 20°C/min, more preferably from 10 to 15°C/min. By setting the temperature rise rate to 5°C/min or higher, abnormal grain growth can be suppressed. By setting the rate to 20°C/min or lower, variations in the temperature within the sintered compact can be suppressed. The temperature is preferably from 1150°C to 1350°C, more preferably from 1200°C to 1350°C. By setting the temperature to 1150°C or higher, the creation of holes in the silicon phase can be suppressed. By setting the temperature to 1350°C or lower, it is possible to suppress melting and an increase in size of the silicon grains. The creation of holes in the silicon phase can also be suppressed by setting the temperature to 1350°C or lower. The pressure is preferably 90 MPa or greater, more preferably 100 MPa or greater. The upper limit value of the pressure is not particularly determined, but is typically 200 MPa. The retention time is preferably from 30 to 240 minutes, more preferably from 60 to 180 minutes, on condition that the temperature and the pressure are within the aforementioned ranges.

[0038]

When sintering by the HIP process is finished, heating is terminated to perform cooling. The cooling method is not particularly limited, and natural cooling is easy and convenient. By appropriately adjusting the aforementioned conditions, the intended target can be obtained successfully.

[0039]

The sputtering target produced as above can suitably be used, for example, for forming a light semi-transmissive film (half-tone phase-shifting film) of a mask blank, which serves as a precursor for producing a half-tone phase-shifting mask. For the substrate to be subjected to sputtering, it is possible to suitably use, for example, a light-transmissive substrate such as transparent silica glass.

Examples

[0040]

The present invention is described in further detail below according to Examples. The scope of the present invention, however, is not limited to those Examples.

[0041]

Example 1:

(1) Preparation of Powder Mixture for Sintering:

An elemental silicon powder having a specific surface area of $4.1 \text{ m}^2/\text{g}$ according to the BET method and an elemental molybdenum powder having a specific surface area of $4.7 \text{ m}^2/\text{g}$ according to the BET method were measured such that the ratio therebetween was Mo:Si = 4:96 (molar ratio). An Attritor (registered trademark) from Nippon Coke & Engineering Co., Ltd. was used to mix the powders, to obtain a powder mixture. The Attritor (registered trademark) was operated at 280 rpm for 24 hours. Zirconia balls having a diameter of 10 mm were used as the medium. The obtained powder mixture was sifted with a sieve having a mesh opening of $50 \text{ }\mu\text{m}$. The sifted powder mixture was pre-sintered at 800°C for 3 hours.

[0042]

(2) Sintering by SPS Process:

The pre-sintered powder mixture was charged into a graphite-made sintering die. The sintering die had a diameter of 230 mm. Then, the powder mixture was sintered by a SPS process. The execution conditions for the SPS process were as follows.

Sintering atmosphere: vacuum (absolute pressure: 10 Pa);

Temperature rise rate: $10^\circ\text{C}/\text{min}$;

Sintering temperature: 1175°C;
Sintering retention time: 30 minutes;
Pressure: 41 MPa;
Temperature drop: natural furnace cooling.

[0043]

Sintering by HIP Process:
Gas: argon;
Temperature rise rate: 10°C/min;
Sintering temperature: 1250°C;
Sintering retention time: 120 minutes;
Pressure: 145 MPa;
Temperature drop: natural furnace cooling.

[0044]

Comparative Example 1:

No HIP process was performed in Example 1. Except therefor, a sputtering target was obtained in like manner as in Example 1.

[0045]

Example 2:

A sputtering target was obtained in like manner as in Example 1, except that the conditions shown in Table 1 below were adopted.

[0046]

Comparative Example 2:

No HIP process was performed in Example 2. Except therefor, a sputtering target was obtained in like manner as in Example 1.

[0047]

Comparative Example 3:

This Comparative Example is an example in which the HIP process in Example 2

was performed according to the conditions shown in Table 1 below. Except therefor, a sputtering target was obtained in like manner as in Example 2.

[0048]

Example 3:

A sputtering target was obtained in like manner as in Example 1, except that the conditions shown in Table 1 below were adopted.

[0049]

Comparative Example 4:

This Comparative Example is an example in which sintering according to a HP process according to the conditions shown in Table 1 was performed, instead of the SPS process. Except therefor, a sputtering target was obtained in like manner as in Example 3.

[0050]

Example 4:

A sputtering target was obtained in like manner as in Example 1, except that the conditions shown in Table 1 below were adopted.

[0051]

Comparative Example 5:

No HIP process was performed in Example 4. Except therefor, a sputtering target was obtained in like manner as in Example 1.

[0052]

Evaluation:

For each of the targets obtained by the Examples and Comparative Examples, the average grain size of the silicon grains and the average grain size of the molybdenum silicide grains were measured according to the aforementioned method. Further, the number of holes present in the silicon phase and having a major axis of 0.3 μm or greater (within an area of 90 $\times$ 125 μm) was measured. Further, the number of aggregates of

molybdenum silicide grains was measured. Furthermore, the relative density of the target was measured. The results are shown in Table 1 below.

[0053]

[Table 1]

	Si:Mo molar ratio	SPS		HIP		Si average grain size (μm)	MoSi ₂ average grain size (μm)	Number of holes in Si phase (holes/field of view)	Number of MoSi ₂ aggregates (pieces/ mm^2)	Relative density (%)
		Temperature ($^{\circ}\text{C}$)	Pressure (MPa)	Temperature ($^{\circ}\text{C}$)	Pressure (MPa)					
Example 1	96:4	1175	41	1250	145	1.60	1.99	0.9	0	100.1
Comparative Example 1	96:4	1175	41	-	-	1.43	1.92	11.3	0	99.6
Example 2	96:4	1195	41	1270	145	1.79	2.10	1.2	0	100.1
Comparative Example 2	96:4	1195	41	-	-	1.70	2.07	31.9	0	99.7
Comparative Example 3	96:4	1195	41	1370	145	2.12	2.63	39.2	2	99.7
Example 3	87:13	1155	28	1330	100	1.20	1.60	0.4	0	100.5
Comparative Example 4	87:13	HP 1330	28	1330	100	3.13	2.15	13.4	4	99.0
Example 4	75:25	1135	41	1210	145	1.69	1.76	1.5	0	100.7
Comparative Example 5	75:25	1135	41	-	-	1.50	1.71	17.8	0	99.8

[0054]

The results of Table 1 show that all of the targets of Examples 1 to 4 include a silicon phase in which the average grain size of silicon grains is 2.0 μm or less and a molybdenum silicide phase in which the average grain size of molybdenum silicide grains is 2.5 μm or less, and the average number of holes present in the silicon phase and having a major axis of 0.3 μm or greater is ten or fewer within an area of 90 $\times$ 125 μm .

[0055]

Next, for the respective sputtering targets of Example 1 and Comparative Example 1, the following evaluation was performed to verify the effects related to particles created when forming a thin film by sputtering using those targets.

[0056]

First, ten pieces of light-transmissive substrates made of synthetic silica glass were prepared, the dimensions of the substrate's principal surface being approximately 152 mm wide and approximately 152 mm long and the thickness being approximately 6.25 mm. The end surfaces and the principal surface of each light-transmissive substrate were polished to a predetermined surface roughness, and then were subjected to predetermined cleaning and drying processes. Next, for each of the prepared light-transmissive substrates, the principal surface on the side for forming a thin film was subjected to defect inspection with a defect inspecting device (M6640 from Lasertec Corporation). In this defect inspection, for each inspected light-transmissive substrate, defect data about the types of defects (projecting defects, depressed defects, etc.) and the positions (coordinates) of the respective defects present on the principal surface on the side for forming a thin film were obtained, and the data were recorded in association with the light-transmissive substrate subjected to the defect inspection.

[0057]

Next, the light-transmissive substrates having been subjected to defect inspection were divided into two sets, each set including five substrates. Onto each of the light-transmissive substrates in one set, a thin film was formed by sputtering using the sputtering target of Example 1, to produce thin film-equipped substrates according to

Example 1. Onto each of the light-transmissive substrates in the other set, a thin film was formed by sputtering using the sputtering target of Comparative Example 1, to produce thin film-equipped substrates according to Comparative Example 1.

[0058]

More specifically, the following steps were performed. The sputtering target of Example 1 or Comparative Example 1 was attached to the cathode inside a film forming chamber of a single-substrate DC sputtering device, and a light-transmissive substrate was placed on a substrate stage inside the film forming chamber such that the principal surface subjected to defect inspection faced the sputtering target. Next, an atmosphere of a mixed gas of argon (Ar), nitrogen (N₂), and helium (He) (gas flow rates: 10.5 sccm for Ar, 48 sccm for N₂, 100 sccm for He; gas pressure: 0.3 Pa) was formed inside the film forming chamber, and reactive sputtering was performed by setting the power of the DC power source to 3.0 kW, to thereby form a 67-nm-thick thin film made of molybdenum, silicon, and nitrogen on the principal surface of the light-transmissive substrate. In this way, a thin film-equipped substrate according to Example 1 or Comparative Example 1 was produced.

[0059]

Next, the surface of the thin film on each thin film-equipped substrate according to Example 1 and each thin film-equipped substrate according to Comparative Example 1 was subjected to defect inspection with a defect inspecting device (M6640 from Lasertec Corporation). Also in this defect inspection, defect data about the types of defects (projecting defects, depressed defects, etc.) and the positions (coordinates) of the respective defects present on the surface of the inspected thin film were obtained, and the data were recorded in association with the thin film-equipped substrate (light-transmissive substrate) subjected to the defect inspection.

[0060]

Finally, each of the thin film-equipped substrates according to Example 1 and Comparative Example 1 was subjected to an operation of extracting only the defects that were created while forming the thin film by sputtering. More specifically, the defect

data of the principal surface of the light-transmissive substrate and the defect data of the surface of the thin film which were associated with the same light-transmissive substrate were compared; defects that were present at the same positions (coordinates) in the two pieces of defect data were eliminated from the defect data of the surface of the thin film; and this data was recorded in association with that thin film-equipped substrate (light-transmissive substrate) as defect data regarding defects (film defects) created upon thin film formation.

[0061]

From these verification results, it was verified that the average number of film defects of the five thin film-equipped substrates according to Example 1 was reduced to one-twenty fifth ($1/25$) of the average number of film defects of the five thin film-equipped substrates according to Comparative Example 1. These results show that, by forming a thin film by sputtering by using the sputtering target of Example 1, it is possible to sufficiently suppress the creation of particles from the sputtering target due to arcing upon sputtering.

Industrial Applicability

[0062]

According to the present invention, it is possible to provide a Mo-Si-based sputtering target in which the creation of particles is suppressed compared to conventional art, and a method for producing the sputtering target.

CLAIMS

1. A sputtering target comprising

a molybdenum content of from 3 to 25 mol% and

a silicon content of from 75 to 97 mol%, wherein:

the sputtering target includes a silicon phase in which an average grain size of silicon grains is 2.0 μm or less, and a molybdenum silicide phase in which an average grain size of molybdenum silicide grains is 2.5 μm or less; and

an average number of holes present at a magnification of 5000x in the silicon phase and having a major axis of 0.3 μm or greater is ten or fewer within an area of $90 \times 125 \mu\text{m}$, and wherein the sputtering target has a relative density of 100% or more.

2. The sputtering target according to claim 1, wherein the number of aggregates created by aggregation of the molybdenum silicide grains and having a circle-equivalent diameter of 10 μm or greater is one or fewer per 1 mm^2 .

3. A production method for producing the sputtering target according to any one of claims 1 or 2, the method comprising steps of:

mixing a molybdenum powder and a silicon powder;

subjecting the obtained powder mixture to a spark plasma sintering process; and

then

subjecting the powder mixture to a hot isostatic pressing process, wherein,

in the step of subjecting the powder mixture to the hot isostatic pressing process, the sintering temperature is from 1150°C to 1350°C.

4. The production method according to claim 3, wherein, in the step of subjecting the powder mixture to the spark plasma sintering process, the sintering temperature is from 1100°C to 1200°C.