

DESCRIPTION

COPPER ALLOY SPUTTERING TARGET AND MANUFACTURING METHOD OF
SAID TARGET

BACKGROUND OF THE INVENTION

Technical Field

The present invention pertains to a copper alloy sputtering target capable of forming an interconnection material of a semiconductor device, particularly a stable and even seed layer during electroplating, and superior in sputtering deposition characteristics. The present invention also pertains to the manufacturing method of such a target.

Background Art

Conventionally, although Al (resistivity of roughly $3.1 \mu \Omega \cdot \text{cm}$) has been used as the interconnection material of a semiconductor device, low-resistivity copper interconnection (resistivity of roughly $1.7 \mu \Omega \cdot \text{cm}$) has been put into practical application pursuant to the miniaturization of wiring.

As the current formation process of copper interconnection, after forming a diffusion barrier layer such as Ta/TaN to the concave portion of a contact hole or wiring groove, copper electroplating is often performed thereto. As the base layer (seed layer) for performing this electroplating, sputtering deposition is generally performed to copper or copper alloy.

The even formation of this base layer is important, and, if the base layer agglomerates, an even film cannot be formed upon forming a copper film with electroplating. For instance, defects such as voids, hillocks, disconnections and so on may be formed during the wiring.

Further, even if defects such as a void are not formed, an uneven copper electrodeposit will be formed at this portion, and a problem will arise in that the electromigration resistance characteristics will deteriorate.

In order to overcome this problem, it is important to form a stable and even seed layer during copper electroplating, and a sputtering target having superior sputtering deposition characteristics and being optimum for forming a seed layer will be required.

therefor.

Heretofore, as the copper interconnection material, a proposal has been made of adding certain elements to copper so as to improve the electromigration (EM) resistance characteristics, corrosion resistance, bond strength, and so on. For example, Japanese Patent Laid-Open Publication No. H5-311424 and Japanese Patent Laid-Open Publication No. H10-60633 disclose a pure copper target or a target to which 0.04 to 0.15wt% of Ti is added to the pure copper.

And, in these proposals, it is proposed that rapid cooling be performed for the even dispersion of the added elements, or continuous casting be performed for preventing the segregation of the added elements in an ingot, ingot piping during casting, or enlargement of the crystal grains of the ingot.

Nevertheless, even if high purity copper is used alone or with minute amounts of metal added thereto, although there is an advantage in that the resistivity will be low, problems regarding electromigration and oxidation resistance during the process still remain, and these materials are not necessarily favorable materials.

In particular, since the aspect ratio is becoming higher (aspect ratio of 4 or higher) in recent days, sufficient electromigration resistance and oxidation resistance are required.

In light of the above, although a copper alloy sputtering target formed from high purity copper or with certain elements added thereto has been proposed, conventionally, this was not exactly sufficient.

Disclosure of the Invention

Accordingly, an object of the present invention is to provide a copper alloy sputtering target capable of forming an interconnection material of a semiconductor device, particularly a stable and even seed layer during electroplating, and superior in sputtering deposition characteristics. Another object of the present invention is to provide a manufacturing method of such a target.

In order to achieve the foregoing objects, as a result of conducting intense study, the present inventors have discovered that, as a result of adding a suitable amount of metal elements, it is possible to obtain a copper alloy sputtering target capable of preventing the generation of defects such as voids, hillocks and disconnections during copper electroplating, which has low resistivity, which has electromigration resistance and oxidization resistance characteristics, and which is able to form a stable and even seed layer.

Based on the foregoing discovery, the present invention provides:

1. A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, wherein said target contains 0.4 to 5wt% of Sn, the structure of the target does not substantially contain any precipitates, and the resistivity of the target material is $2.3 \mu \Omega \text{ cm}$ or more;
2. A copper alloy sputtering target according to paragraph 1 above, wherein said target contains 0.5 to 1wt% of Sn;
3. A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, wherein said target contains 0.2 to 5wt% of Al, the structure of the target does not substantially contain any precipitates, and the resistivity of the target material is $2.2 \mu \Omega \text{ cm}$ or more;
4. A copper alloy sputtering target according to paragraph 3 above, wherein said target contains 0.5 to 1wt% of Al;
5. A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, wherein said target contains 0.3 to 5wt% of Ti, the structure of the target does not substantially contain any precipitates, and the resistivity of the target material is $9 \mu \Omega \text{ cm}$ or more;
6. A copper alloy sputtering target according to paragraph 5 above, wherein said target contains 0.5 to 1wt% of Ti;
7. A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, wherein said target contains a total of 0.2 to 5wt% of at least one component selected from Sn, Al and Ti, the structure of the target does not substantially contain any precipitates, and the resistivity of the target material is greater than the resistivity of the copper alloy having the same composition in a thermal equilibrium state;
8. A copper alloy sputtering target according to paragraph 7 above, wherein said target contains a total of 0.5 to 1wt% of at least one component selected from Sn, Al and Ti;
9. A copper alloy sputtering target according to paragraph 7 or paragraph 8, wherein the increase in resistivity due to the alloying element is resistivity that is 1.2 times or more than that of the thermal equilibrium;
10. A copper alloy sputtering target according to any one of paragraphs 1 to 9 above, wherein Na and K are respectively 0.5ppm or less; Fe, Ni, Cr and Ca are respectively 2ppm or less; U and Th are respectively 1ppb or less, oxygen is 5ppm or less, hydrogen is 2ppm

less;

11. A copper alloy sputtering target according to any one of paragraphs 1 to 9 above, wherein Na and K are respectively 0.1ppm or less; Fe, Ni, Cr and Ca are respectively 1ppm or less; U and Th are respectively 1ppb or less, oxygen is 5ppm or less, hydrogen is 2ppm or less; and unavoidable impurities excluding alloying additional elements are 10ppm or less;

12. A copper alloy sputtering target according to any one of paragraphs 1 to 11 above, wherein the crystal grain size of the target material is 50 μ m or less, and the variation in the average grain size by location is within $\pm 20\%$;

13. A copper alloy sputtering target according to any one of paragraphs 1 to 12 above, wherein the variation in the alloying element of the target material within 0.2%;

14. A copper alloy sputtering target according to any one of paragraphs 1 to 13 above, wherein, when the alloy contains Al, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or more in the sputtering face, and, when the alloy contains Sn and/or Ti, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or less in the sputtering face, and the variation in $I(111)/I(200)$ in the sputtering face is respectively within $\pm 30\%$; and

15. A manufacturing method of a copper alloy sputtering target according to any one of paragraphs 1 to 14 above, comprising the steps of performing hot forging and/or hot rolling to a high purity copper alloy ingot obtained by vacuum melting; further performing cold rolling thereto; and thereafter sandwiching this with copper plates underwater and performing forced cooling thereto during heat treatment.

Best Mode for Carrying Out the Invention

The copper alloy sputtering target of the present invention contains a 0.4 to 5wt%, preferably 0.5 to 1wt% of Sn; 0.2 to 5wt%, preferably 0.5 to 1wt% of Al; 0.3 to 5wt%, preferably 0.5 to 1wt% of Ti; respectively, or a total of 0.2 to 5wt% of at least one component selected from Sn, Al and Ti.

When 0.4 to 5wt% of Sn is independently added, resistivity of the target material will be 2.3 $\mu \Omega$ cm or more; when 0.2 to 5wt% of Al is independently added, resistivity of the target material will be 2.2 $\mu \Omega$ cm or more, and when 0.3 to 5wt% of Ti is independently added, resistivity of the target material will be 9 $\mu \Omega$ cm or more. Further, when these are

mixed and added, resistivity of the target material will be $2.2 \mu \Omega \text{ cm}$ or more. These may be suitably selected and used for the formation of a seed layer during copper electroplating.

Although the structure of the copper alloy sputtering target of the present invention does not substantially contain any precipitates, when the foregoing additive amount of alloy exceeds 0.2wt%, precipitates will arise during the manufacture process of the target.

When precipitates exist in the target structure, particles will be generated since the sputtering rate between the matrix phase and precipitate phase will differ, and problems such as wiring disconnections in the semiconductor device will occur.

In particular, it has become evident that these precipitates are formed in the center (middle) of the target separate from the surface, and not near the target surface.

Therefore, problems caused by precipitates occur not during the initial phase of sputtering, but from a stage in which the erosion of the target caused by sputtering has progressed to a certain degree. In other words, precipitates are caused by minute particles getting mixed into the sputtering film, or due to the micro unevenness of the film composition midway during sputtering.

As a matter of course, since such uneven portions of the seed film generate uneven electric fields, the copper plating film structure will become uneven and minute, and electromigration resistance characteristics will deteriorate, which is obviously unfavorable. Although the problem is often overlooked since it does not occur in the initial stages, this is a major problem.

In light of the above, in order to confirm the existence of precipitates in the target, it is insufficient to search only the mechanical strength characteristics such as the resistivity value and hardness of the target surface with the likes of XRD, and it is necessary to also search the inside of the target with high resolution SEM.

Further, with the copper alloy sputtering target of the present invention, it is desirable that Na and K are respectively 0.5ppm or less, preferably 0.1ppm or less; Fe, Ni, Cr and Ca are respectively 2ppm or less, preferably 1ppm or less; U and Th are respectively 1ppb or less, oxygen is 5ppm or less, hydrogen is 2ppm or less; and unavoidable impurities excluding alloying additional elements are 50ppm or less. These elements are harmful components that may diffuse and contaminate the semiconductor device.

It is preferable that the crystal grain size of the target material is $50 \mu \text{m}$ or less, and the variation in the average grain size by location is within $\pm 20\%$. The crystal grain size of the target and variations in the average grain size by location will affect the evenness of the film thickness.

the target and variations in the average grain size by location will affect the uniformity of the film thickness.

Moreover, when the variation is significant in the alloy elements of the target material, the characteristic values of the target material will change and therefore cause the interconnection material of the semiconductor device, particularly the resistivity of the seed layer, to change, and it is desirable that the variation be within 0.2%.

Further, orientation of the crystal will also affect the uniformity of the film thickness. Generally, although it is considered that a random orientation is favorable, depending on the type of additive element, a specific crystal orientation with the variation being within a certain range will yield a further superior uniformity of the film thickness.

In other words, when the alloy contains Al, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or more in the sputtering face, and, when the alloy contains Sn and/or Ti, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or less in the sputtering face. And, when the variation in $I(111)/I(200)$ in the sputtering face is respectively within $\pm 30\%$, the film thickness standard deviation σ will be 1.5% or less, and a copper alloy sputtering target superior in uniformity of the film thickness can be obtained thereby.

Further, upon manufacturing the target, after performing homogenization heat treatment with a certain degree of thickness, in the subsequent cooling step, it is important to sandwich this with metals having a large thermal capacity such as copper plates underwater, and to increase the cooling effect without generating a vapor layer on the surface thereof. This is because if a vapor layer is formed, the cooling effect will significantly deteriorate.

Examples and Comparative Examples

The present invention is now explained in detail with reference to the Examples. These Examples are merely illustrative, and the present invention shall in no way be limited thereby. In other words, various modifications and other embodiments based on the technical spirit claimed in the claims shall be included in the present invention as a matter of course.

(Example 1-1)

Electrolytic copper (purity of 99.95%) was subject to electrolytic refining in nitric solution so as to differentiate anodes from cathodes with a diaphragm such that it became a

purity of 99.9999%. 1.0wt% of Sn (purity of 99.9999%) was added thereto, and this was subject to vacuum melting in order to prepare a high purity copper alloy ingot (ϕ 160×60t) containing 1.0wt% of Sn.

This ingot was heated to 400°C and subject to hot forging such that it became ϕ 190×40t. Further, this was heated to 400°C and rolled until it became ϕ 265×20t. Thereafter, this was rolled until it became ϕ 360×10t with cold rolling, heat treatment was performed thereto at 500°C for 1 hour, and this was sandwiched with copper plates under water for forced cooling.

Moreover, this was machine processed to obtain a discoid target having a diameter of 13 inches and a thickness of 7mm.

(Example 1-2)

Electrolytic copper (purity of 99.95%) was subject to electrolytic refining in nitric solution so as to differentiate anodes from cathodes with a diaphragm such that it became a purity of 99.9999%. 0.5wt% of Sn (purity of 99.9999%) was added thereto, and this was subject to vacuum melting in order to prepare a high purity copper alloy ingot (ϕ 160×60t) containing 0.5wt% of Sn.

With the other conditions being the same as Example 1-1, a copper alloy target containing 0.5wt% of Sn was prepared.

(Comparative Example 1-1)

Using the same materials as Example 1-1, after performing heat treatment at 500 degrees for 1 hour, this was cooled in a furnace. The other conditions were the same as Example 1-1. As a result, a copper alloy target containing 1.0wt% of Sn was prepared.

(Comparative Example 1-2)

Using the same materials as Example 1-2, after performing heat treatment at 500 degrees for 1 hour, this was cooled in a furnace. The other conditions were the same as Example 1-2. As a result, a copper alloy target containing 0.5wt% of Sn was prepared.

(Example 2-1)

Electrolytic copper (purity of 99.95%) was subject to electrolytic refining in nitric solution so as to differentiate anodes from cathodes with a diaphragm such that it became a purity of 99.9999%. 1.0wt% of Al (purity of 99.9999%) was added thereto, and this was subject to vacuum melting in order to prepare a high purity copper alloy ingot (ϕ 160×60t) containing 1.0wt% of Al.

This ingot was heated to 400°C and subject to hot forging such that it became ϕ

190×40t. Further, this was heated to 400°C and rolled until it became ϕ 265×20t.

Thereafter, this was rolled until it became ϕ 360×10t with cold rolling, heat treatment was performed thereto at 500°C for 1 hour, and this was sandwiched with copper plates under water for forced cooling. Moreover, this was machine processed to obtain a discoid target having a diameter of 13 inches and a thickness of 7mm.

(Example 2-2)

Electrolytic copper (purity of 99.95%) was subject to electrolytic refining in nitric solution so as to differentiate anodes from cathodes with a diaphragm such that it became a purity of 99.9999%. 0.5wt% of Al (purity of 99.9999%) was added thereto, and this was subject to vacuum melting in order to prepare a high purity copper alloy ingot (ϕ 160×60t) containing 0.5wt% of Al.

With the other conditions being the same as Example 2-1, a copper alloy target containing 0.5wt% of Al was prepared.

(Comparative Example 2-1)

Using the same materials as Example 2-1, after performing heat treatment at 500 degrees for 1 hour, this was cooled in a furnace. The other conditions were the same as Example 2-1. As a result, a copper alloy target containing 1.0wt% of Al was prepared.

(Comparative Example 2-2)

Using the same materials as Example 2-2, after performing heat treatment at 500 degrees for 1 hour, this was cooled in a furnace. The other conditions were the same as Example 2-2. As a result, a copper alloy target containing 0.5wt% of Al was prepared.

(Example 3-1)

Electrolytic copper (purity of 99.95%) was subject to electrolytic refining in nitric solution so as to differentiate anodes from cathodes with a diaphragm such that it became a purity of 99.9999%. 1.0wt% of Ti (purity of 99.9999%) was added thereto, and this was subject to vacuum melting in order to prepare a high purity copper alloy ingot (ϕ 160×60t) containing 1.0wt% of Ti.

This ingot was heated to 400°C and subject to hot forging such that it became ϕ 190×40t. Further, this was heated to 400°C and rolled until it became ϕ 265×20t. Thereafter, this was rolled until it became ϕ 360×10t with cold rolling, heat treatment was performed thereto at 500°C for 1 hour, and this was sandwiched with copper plates under water for forced cooling.

Moreover, this was machine processed to obtain a discoid target having a diameter of 13 inches and a thickness of 7mm.

(Example 3-2)

Electrolytic copper (purity of 99.95%) was subject to electrolytic refining in nitric solution so as to differentiate anodes from cathodes with a diaphragm such that it became a purity of 99.9999%. 0.5wt% of Ti (purity of 99.9999%) was added thereto, and this was subject to vacuum melting in order to prepare a high purity copper alloy ingot (ϕ 160×60t) containing 0.5wt% of Ti.

With the other conditions being the same as Example 3-1, a copper alloy target containing 0.5wt% of Ti was prepared.

(Comparative Example 3-1)

Using the same materials as Example 3-1, after performing heat treatment at 500 degrees for 1 hour, this was cooled in a furnace. The other conditions were the same as Example 3-1. As a result, a copper alloy target containing 1.0wt% of Ti was prepared.

(Comparative Example 3-2)

Using the same materials as Example 3-2, after performing heat treatment at 500 degrees for 1 hour, this was cooled in a furnace. The other conditions were the same as Example 3-2. As a result, a copper alloy target containing 0.5wt% of Ti was prepared.

(Evaluation Results of Examples 1-1 to 3-2 and Comparative Examples 1-1 to 3-2)]

With respect to the targets prepared in foregoing Examples 1-1 to 3-2 and Comparative Examples 1-1 to 3-2, measurement, observation, research and so on regarding the resistivity ($\mu\Omega \cdot \text{cm}$), precipitates, crystal grain size, variation, existence of voids, hillocks and disconnections were conducted. The results are shown in Table 1. Further, the analysis results of impurities of the targets are shown in Table 2.

Further, the crystal grain size was calculated with the method of section prescribed in JIS H0501, and the variation was calculated by radially measuring 17 points (center, and 8 points of 1/2R and 8 points of R) of the sputtering face of the target. Moreover, the existence of precipitates was searched with high resolution SEM.

The resistivity was calculated by measuring 17 points, respectively, in the upper face, lower face and middle face of the target with the four-terminal method. Regarding the EM characteristics evaluation, after depositing a Ta/TaN diffusion barrier to a wiring groove having a wiring width of $0.2\mu\text{m}$ and depth of $0.8\mu\text{m}$, a copper alloy seed film of $500\text{\AA}$ (deposition film thickness on a flat substrate) was formed on each of the various targets

described above. Thereafter, with copper containing phosphorus as the anode, a copper film was embedded with the electroplating method, and excess film at the upper part was removed with the CMP method. Thereafter, annealing was performed at 400°C in an Ar gas atmosphere, current having a current density of 10^{12} /ampere was applied to the wiring net for 1 hour in order to observe the existence of voids and hillocks in the wiring as electromigration (EM) characteristics.

Further, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face which corresponds to Example 1-1 and Example 1-2 is shown in Table 3, the ratio of $I(111)/I(200)$ corresponding to Example 2-1 and Example 2-2 is shown in Table 4, and the ratio of $I(111)/I(200)$ corresponding to Examples 3-1 and Example 3-2 is shown in Table 5, respectively.

Moreover, the influence (film thickness standard deviation σ (%)) of the ratio $I(111)/I(200)$ with the X-ray diffraction peak intensity $I(200)$ on the film thickness distribution is shown in Table 6. Here, the variation of $I(111)/I(200)$ in the sputtering face was all within $\pm 30\%$.

As a comparison, Comparative Examples 1-1 to 3-4 are also shown. Comparative Examples 2-3 and 2-4 are targets in which the final heat treatment was not performed, and Comparative Examples 1-3, 1-4, 3-3 and 3-4 are cases where the heat treatment temperature was set to 750°C for 1 hour.

Table 1

	Target	Resistivity ($\mu\Omega \cdot \text{cm}$)	Precipitates	Grain Size (μm)	Variation ($\pm\%$)	Existence of Voids	Existence of Hillocks	Disconnections
Examples 1-1	Cu+1.0%Sn	3.3	Not Observed	23	15	None	None	None
Comparative Examples 1-1	Cu+1.0%Sn	2.7	Small Amount	68	26	Existed	Existed	None
Examples 1-2	Cu+0.5%Sn	2.5	Not Observed	22	11	None	None	None
Comparative Examples 1-2	Cu+0.5%Sn	2.1	Small Amount	48	12	Existed	Existed	Existed
Examples 2-1	Cu+1.0%Al	4.3	Not Observed	39	11	None	None	None
Comparative Examples 2-1	Cu+1.0%Al	3.8	Small Amount	85	34	Existed	Existed	None
Examples 2-2	Cu+0.5%Al	2.8	Not Observed	45	19	None	None	None
Comparative Examples 2-2	Cu+0.5%Al	2.2	Small Amount	95	42	Existed	Existed	None
Examples 3-1	Cu+1.0%Ti	15.1	Not Observed	29	13	None	None	None
Comparative Examples 3-1	Cu+1.0%Ti	12.6	Small Amount	58	18	Existed	Existed	Existed
Examples 3-2	Cu+0.5%Ti	13.2	Not Observed	36	9	None	None	None
Comparative Examples 3-2	Cu+0.5%Ti	10.5	Small Amount	41	26	Existed	Existed	None

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Table 2

	Example 1-1	Comparative Example 1-1	Example 1-2	Comparative Example 1-2	Example 2-1	Comparative Example 2-1
Sn	—	—	—	—	0.01	0.01
Al	0.03	0.03	0.02	0.02	—	—
Ti	0.03	0.03	0.03	0.03	0.03	0.03
Na	0.01	0.01	0.01	0.01	0.01	0.01
K	0.01	0.01	0.02	0.02	0.01	0.01
Fe	0.08	0.08	0.09	0.09	0.02	0.02
Ni	0.06	0.06	0.05	0.05	0.008	0.008
Cr	0.04	0.04	0.04	0.04	0.005	0.005
Ca	0.01	0.01	0.01	0.01	0.005	0.005
C	10	10	8	8	10	10
O	10	10	7	7	10	10
H	1	1	1	1	1	1
Ag	0.27	0.27	0.23	0.23	0.3	0.3
Zr	0.005	0.005	0.005	0.005	0.01	0.01
Hf	0.001	0.001	0.001	0.001	0.001	0.001
U	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Th	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001

	Example 2-2	Comparative Example 2-2	Example 3-1	Comparative Example 3-1	Example 3-2	Comparative Example 3-2
Sn	0.02	0.02	0.04	0.04	0.04	0.04
Al	—	—	0.13	0.13	0.11	0.11
Ti	0.01	0.01	—	—	—	—
Na	0.01	0.01	0.01	0.01	0.01	0.01
K	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.03	0.03	0.1	0.1	0.1	0.1
Ni	0.01	0.01	0.03	0.03	0.05	0.05
Cr	0.004	0.004	0.03	0.03	0.01	0.01
Ca	0.003	0.003	0.05	0.05	0.03	0.03
C	9	9	10	10	8	8
O	8	8	10	10	9	9
H	1	1	1	1	1	1
Ag	0.23	0.23	0.33	0.33	0.22	0.22
Zr	0.02	0.02	0.01	0.01	0.01	0.01
Hf	0.001	0.001	0.001	0.001	0.001	0.001
U	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Th	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001

Table 3

Cu-1wt%Sn (Corresponds to Example 1-1))

	1	2	3	4	5	6	7	8	9
(111)	3602	3121	1782	2866	1971	2103	2866	2133	2966
(200)	1915	1469	1347	1538	1422	1137	1255	1194	1499
(220)	591	727	1024	587	982	793	913	608	816
(311)	794	725	728	680	569	733	683	591	709
(111)/(200)	1.88	2.12	1.32	1.86	1.39	1.85	2.28	1.79	1.98

Cu-0.5wt%Sn (Corresponds to Example 1-2)

	1	2	3	4	5	6	7	8	9
(111)	3510	2960	1586	2768	2709	2814	2696	2812	2613
(200)	1924	1528	1354	1643	1647	1598	1637	1635	1621
(220)	623	745	1031	602	601	587	587	560	593
(311)	814	702	701	667	690	683	677	680	653
(111)/(200)	1.82	1.94	1.17	1.68	1.64	1.76	1.65	1.72	1.61

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Table 4

Cu-1wt%Al (Corresponds to Example 2-1)

	1	2	3	4	5	6	7	8	9
(111)	21421	16109	17788	24298	23122	21366	19688	21223	19883
(200)	9024	8697	7570	8466	8326	7366	6398	8011	6759
(220)	3107	5249	3713	2850	6216	4469	2964	2633	3987
(311)	3970	3266	3690	3700	3169	3322	3126	3770	3445
(111)/(200)	2.37	1.85	2.35	2.87	2.78	2.90	3.08	2.65	2.94

Cu-0.5wt%Al (Corresponds to Example 2-2)

	1	2	3	4	5	6	7	8	9
(111)	29341	27830	26552	30444	22078	25913	25215	26319	31025
(200)	12085	11620	11271	12027	13537	12550	13131	11388	12027
(220)	10458	11330	14816	9528	15687	14176	14525	14467	9703
(311)	6217	7321	5520	6101	6798	5403	5229	5926	5345
(111)/(200)	2.43	2.40	2.36	2.53	1.63	2.06	1.92	2.31	2.58

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Table 5

Cu-1wt%Ti (Corresponds to Example 3-1)

	1	2	3	4	5	6	7	8	9
(111)	2466	3184	1548	2786	2963	3022	1638	2677	2997
(200)	1757	1652	1123	1780	1866	1542	1213	1643	1466
(220)	690	520	1129	513	613	513	544	498	533
(311)	666	709	586	684	658	684	711	644	703
(111)/(200)	1.40	1.93	1.38	1.57	1.59	1.96	1.35	1.63	2.04

Cu-0.5wt%Ti (Corresponds to Example 3-2)

	1	2	3	4	5	6	7	8	9
(111)	2176	3140	1505	2671	2666	2863	1335	2401	2939
(200)	1770	1689	1157	1847	1873	1552	1274	1672	1474
(220)	713	528	1125	512	632	514	546	460	534
(311)	635	720	585	694	672	685	680	641	703
(111)/(200)	1.23	1.86	1.30	1.45	1.42	1.85	1.05	1.44	1.99

Table 6

Cu-Sn	Example 1-1	Example 1-2	Comparative Example 1-3	Comparative Example 1-4
(111)/(200)	1.83	1.67	2.35	3.56
Film Thickness standard deviation σ (%)	1.5	1.1	1.7	1.9

Cu-Al	Example 2-1	Example 2-2	Comparative Example 2-3	Comparative Example 2-4
(111)/(200)	2.64	2.25	1.73	1.21
Film Thickness standard deviation σ (%)	1.3	1.4	1.8	2.6

Cu-Ti	Example 3-1	Example 3-2	Comparative Example 3-3	Comparative Example 3-4
(111)/(200)	1.65	1.51	2.74	3.46
Film Thickness standard deviation σ (%)	1.2	1	1.8	2.3

As clear from Table 1, regarding Examples 1-1 to 3-2, precipitates were not observed, the crystal grain size was within the range of $50\text{ }\mu\text{m}$, the variation was minor, voids and hillocks did not exist, and there were no disconnections.

Contrarily, regarding Comparative Examples 1-1 to 3-2, precipitates were observed, the crystal grain size enlarged, the variation was significant, voids and hillocks existed, and there were disconnections. The results were all inferior in comparison to Examples 1-1 to 3-2.

Further, as shown in Tables 3 to 6, when the alloy contained Al, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face was 2.2 or more in the sputtering face, and, when the alloy contained Sn and/or Ti, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face was 2.2 or less in the sputtering face, the film thickness standard deviation σ was 1.5% or less, and a copper alloy sputtering target having superior evenness in film thickness was obtained thereby. Contrarily, in Comparative Examples 1-3, 1-4, 2-3, 2-4, 3-3 and 3-4, σ exceeded 1.5% in all cases, and resulted in inferior evenness.

Accordingly, it is evident that the copper alloy sputtering target of the present invention possesses favorable characteristics.

Effect of the Invention

The copper alloy sputtering target of the present invention yields superior effects in that it is capable of preventing the generation of defects such as voids, hillocks and disconnections during copper electroplating, it has low resistivity, it has electromigration resistance and oxidization resistance characteristics, and it is able to form a stable and even seed layer.

CLAIMS

1. A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, wherein said target contains 0.4 to 5wt% of Sn, the structure of the target does not substantially contain any precipitates, the resistivity of the target material is $2.3 \mu \Omega \text{ cm}$ or more, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or less in the sputtering face, and the variation in $I(111)/I(200)$ in the sputtering face is respectively within $\pm 30\%$.
2. A copper alloy sputtering target according to claim 1, wherein said target contains 0.5 to 1wt% of Sn.
3. A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, wherein said target contains 0.2 to 5wt% of Al, the structure of the target does not substantially contain any precipitates, the resistivity of the target material is $2.2 \mu \Omega \text{ cm}$ or more, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or more in the sputtering face, and the variation in $I(111)/I(200)$ in the sputtering face is respectively within $\pm 30\%$.
4. A copper alloy sputtering target according to claim 3, wherein said target contains 0.5 to 1wt% of Al.
5. A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, wherein said target contains 0.3 to 5wt% of Ti, the structure of the target does not substantially contain any precipitates, the resistivity of the target material is $9 \mu \Omega \text{ cm}$ or more, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or less in the sputtering face, and the variation in $I(111)/I(200)$ in the sputtering face is respectively within $\pm 30\%$.
6. A copper alloy sputtering target according to claim 5, wherein said target contains 0.5 to 1wt% of Ti.
7. A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, wherein said target contains a total of 0.2 to 5wt% of at least one component selected from Sn, Al and Ti, the structure of the target does not substantially contain any precipitates, and the resistivity of

the target material is greater than the resistivity of the copper alloy having the same composition in a thermal equilibrium state, when the alloy contains Al, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or more in the sputtering face, and, when the alloy contains Sn and/or Ti, the ratio $I(111)/I(200)$ of the X-ray diffraction peak intensity $I(111)$ of the (111) face and the X-ray diffraction peak intensity $I(200)$ of the (200) face is 2.2 or less in the sputtering face, and the variation in $I(111)/I(200)$ in the sputtering face is respectively within $\pm 30\%$.

8. A copper alloy sputtering target according to claim 7, wherein said target contains a total of 0.5 to 1wt% of at least one component selected from Sn, Al and Ti.

9. A copper alloy sputtering target according to claim 7 or claim 8, wherein the increase in resistivity due to the alloying element is resistivity that is 1.2 times or more than that of the thermal equilibrium.

10. A copper alloy sputtering target according to any one of claims 1 to 9, wherein Na and K are respectively 0.5ppm or less; Fe, Ni, Cr and Ca are respectively 2ppm or less; U and Th are respectively 1ppb or less, oxygen is 5ppm or less, hydrogen is 2ppm or less; and unavoidable impurities excluding alloying additional elements are 50ppm or less.

11. A copper alloy sputtering target according to any one of claims 1 to 9, wherein Na and K are respectively 0.1ppm or less; Fe, Ni, Cr and Ca are respectively 1ppm or less; U and Th are respectively 1ppb or less, oxygen is 5ppm or less, hydrogen is 2ppm or less; and unavoidable impurities excluding alloying additional elements are 10ppm or less.

12. A copper alloy sputtering target according to any one of claims 1 to 11, wherein the crystal grain size of the target material is 50 μ m or less, and the variation in the average grain size by location is within $\pm 20\%$.

13. A copper alloy sputtering target according to any one of claims 1 to 12, wherein the variation in the alloying element of the target material is within 0.2%.

14. A manufacturing method of a copper alloy sputtering target according to any one of claims 1 to 13, comprising the steps of performing hot forging and/or hot rolling to a high purity copper alloy ingot obtained by vacuum melting; further performing cold rolling thereto; and thereafter sandwiching this with copper plates underwater and performing forced cooling thereto during heat treatment.

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ABSTRACT

A copper alloy sputtering target most suitable for formation of an interconnection material of a semiconductor device, particularly for formation of a seed layer, characterized in that the target contains 0.4 to 5wt% of Sn, and the structure of the target does not substantially contain any precipitates, and the resistivity of the target material is $2.2 \mu \Omega \text{ cm}$ or more. This target enables formation of an interconnection material of a semiconductor device, particularly a uniform seed layer stable during copper electroplating and is excellent in sputtering deposition characteristics. A method for manufacturing such a target is also disclosed.