containing chromium and silicon as a main component by a sputter method, and subsequently performing heat treatment in a non-oxygen atmosphere at 800°C or lower.

Examples

[0042] Hereinafter, the present invention will be described in further detail with reference to Examples; however, the present invention is not limited to these. Note that measurements in Examples, Reference Examples and Comparative Examples were performed as follows.

[0043] (1) Film Formation Conditions for Cr-Si Film

<Preparation of Sputtering Target>

A Cr powder with a purity of 4N and a Si powder with a purity of 5N were mixed so as to satisfy the composition of a sputtering target in Table 1 and melted in a carbon crucible at a melting temperature of 1,600°C to obtain a melt at 1,600°C. Note that the target composition in Table 1 is the same as the composition of the powders charged. A Cr-Si alloy powder was obtained from the melt by a gas atomization method. The resulting Cr-Si alloy powder was placed in a carbon crucible and pressure-sintered by hot pressing under the following conditions to prepare a Cr-Si sintered body having a desired composition.

(Sintering Conditions)

· Sintering furnace: Hot-press furnace

· Temperature increase rate: 200°C/hour

· Temperature increase atmosphere: Vacuum (5 Pa or less)

· Sintering temperature: 1,250°C

· Sintering pressure: 20 MPa

· Sintering time: 3 hours

The resulting sintered body was machined into a sputtering target with a diameter of four inches.

[0044] <Sputtering Step>

Film formation was performed by a sputtering method using each sputtering target obtained to prepare Cr-Si films of Examples, Reference Examples and Comparative Examples having desired compositions. The Cr-Si films of Examples, Reference Examples and Comparative Examples were formed under the conditions shown in Table 1. The detailed film formation conditions are described below.

(Sputtering Conditions)

· Apparatus: DC magnetron sputtering apparatus (manufactured by ULVAC, Inc.)

· Magnetic field strength: 1,000 Gauss (directly on target, horizontal component)

· Distance between target and substrate: 90 mm

· Substrate temperature: Room temperature (about 25°C)

· Type of introduction gas (sputtering atmosphere): Argon (Ar), or argon and nitrogen (N_2)

· Introduction gas partial pressure: Sputtering was performed at the nitrogen partial pressure ($N_2/(Ar + N_2)$) in Table 1.

· Substrate used: Glass substrate (Corning Incorporated, Eagle XG), 0.8 mm in thickness

· Sputtering power: 200 W (2.5 W/cm^2)

· Target film thickness: 100 nm

Note that, in Table 1, the nitrogen partial pressure ($N_2/(Ar + N_2)$) is indicated as a ratio (%) of N_2 to the total amount of $Ar + N_2$ defined as

$$TCR\ (ppm/°C) = (R - R_{30})/(R_{30} \times (T - 30)) \times 10^6$$

The arithmetic mean of the values of TCR determined in the range of 40°C to 150°C was used as the average TCR.

[0049] (3) Method for Calculating Difference between Maximum Value and Minimum Value of TCR

For the TCR in the range of 40°C to 150°C determined in (2), the difference between the maximum value and the minimum value was determined.

[0050] (Example 1)

A Cr-Si film was formed by a sputtering method under the film formation conditions in Table 1 using the sputtering target having the Cr-Si composition (target composition) in Table 1. The resulting Cr-Si film was subjected to heat treatment under a vacuum (5 Pa or less) at the treatment temperature in Table 2. The average TCR, the maximum value of TCR in the temperatures, the minimum value of TCR in the temperatures, the maximum value - the minimum value of TCR, and the resistivity at 30°C of the resulting Cr-Si film were measured. The results are shown in Table 2.

[0051] (Reference Examples 1, 2, 4, and 6, and Example 9)

Cr-Si films were each produced under the same conditions as those in Example 1 except that the composition of the sputtering target and the film formation conditions (atmosphere gas during film formation (introduction gas), $N_2/(Ar + N_2)$, and the film thickness) were changed to the composition of the sputtering target and the film formation conditions in Table 1, and the heat-treatment temperature of the Cr-Si film was changed to the heat-treatment temperature (treatment temperature in

Table 2) of the Cr-Si film. The average TCR, the maximum value of TCR in the temperatures, the minimum value of TCR in the temperatures, the maximum value - the minimum value of TCR, and the resistivity at 30°C of each of the resulting Cr-Si films were measured. The results are shown in Table 2.

[0052] (Reference Example 3)

A Cr-Si film was obtained under the same conditions as those in Example 1 except that, in the preparation of the sputtering target, the temperature of the melt in the gas atomization method was changed to 1,700°C and the sintering temperature in the preparation of the sintered body was changed to 1,350°C, the composition of the sputtering target and the film formation conditions were changed to the composition of the sputtering target and the film formation conditions in Table 1, and heat treatment after the film formation was not performed.

[0053] (Example 5)

A Cr-Si film was obtained under the same conditions as those in Example 1 except that, in the preparation of the sputtering target, the temperature of the melt in the gas atomization method was changed to 1,700°C and the sintering temperature in the preparation of the sintered body was changed to 1,350°C, the composition of the sputtering target and the film formation conditions were changed to the composition of the sputtering target and the film formation conditions in Table 1, and the heat-treatment temperature of the Cr-Si film was changed to the heat-treatment temperature (treatment temperature in Table 2) of the Cr-Si film.

[0054] (Reference Example 5)

A Cr-Si film was obtained in the same manner as in Example 1

and the resistivity at 30°C of the resulting Cr-Si film were measured. The results are shown in Table 2.

[0057] [Table 1]

	Target composition		Film formation conditions		
	Cr (wt%)	Si (wt%)	Introduction gas	$N_2/(Ar + N_2)$ (%)	Film thickness (nm)
Example 1	42	58	Ar, N_2	10	102
Reference Example 1	42	58	Ar, N_2	5	100
Reference Example 2	42	58	Ar	0	97
Reference Example 3	60	40	Ar	0	96
Example 5	60	40	Ar, N_2	10	93
Reference Example 4	25	75	Ar	0	95
Reference Example 5	66	34	Ar	0	93
Reference Example 6	33	67	Ar	0	92
Example 9	33	67	Ar, N_2	10	94
Comparative Example 1	18	82	Ar	0	101
Comparative Example 2	18	82	Ar, N_2	10	97
Comparative Example 3	75	25	Ar	0	96
Comparative Example 4	42	58	Ar, N_2	15	99

[0058] [Table 2]

	Cr (wt%)	Si (wt%)	N (wt%)	Cr /(Cr + Si) (mass ratio)	Si - N (wt%)	Treatment temperature (°C)	Average TCR (ppm/°C)	Maximum value of TCR in temperatures (ppm/°C)	Minimum value of TCR in temperatures (ppm/°C)	Maximum value - minimum value of TCR (ppm/°C)	Resistivity at 30°C (Ω·cm)
Example 1	39.5	46.2	14.3	0.46	31.9	580	-2.5	1.0	-5.8	6.8	1.3E-03
Reference Example 1	42.5	50.3	7.2	0.46	43.1	480	-40.3	-25.7	-52.9	27.2	8.0E-04
Reference Example 2	46.6	53.4	0.0	0.47	53.4	230	23.7	67.0	-28.0	95.0	1.1E-03
Reference Example 3	66.2	33.8	0.0	0.66	33.8	-	6.4	12.6	1.5	11.1	2.1E-04
Example 5	61.9	31.6	6.5	0.66	25.1	530	-5.1	-0.4	-10.6	10.2	7.3E-04
Reference Example 4	27.6	72.4	0.0	0.28	72.4	600	-6.2	37.3	-60.1	97.4	3.8E-02
Reference Example 5	71.2	28.8	0.0	0.71	28.8	-	31.5	85.2	24.5	60.7	1.8E-04
Reference Example 6	37.3	62.7	0.0	0.37	62.7	570	-38.1	8.8	-91.0	99.8	5.3E-03
Example 9	34.0	57.0	9.0	0.37	48.0	660	-1.4	5.6	-17.2	22.8	3.6E-03
Comparative Example 1	20.9	79.1	0.0	0.21	79.1	600	-1410	-1331	-1470	139	9.5E-03
Comparative Example 2	16.0	60.4	23.6	0.21	36.8	600	-1952	-1687	-2160	473	1.1E-01
Comparative Example 3	81.3	18.8	0.0	0.81	18.8	-	92.4	219.0	76	143	1.2E-04
Comparative Example 4	35.5	42.0	22.5	0.46	19.5	600	-281	-260	-298	38	7.2E-02

CLAIMS

[Claim 1] A Cr-Si film comprising chromium (Cr) and silicon (Si), wherein a composition range of the film is Cr/(Cr + Si) = 0.25 to 0.75, and absolute values of TCR in increments of 10°C in a temperature range of 40°C to 150°C are each 0 ppm/°C or more and 100 ppm/°C or less, wherein an absolute value of an average TCR in increments of 10°C in the temperature range is 0 ppm/°C or more and 30 ppm/°C or less, and further comprising nitrogen (N).

[Claim 2] The Cr-Si film according to claim 1, wherein a difference between a maximum value and a minimum value of TCR in increments of 10°C in the temperature range is 100 ppm/°C or less.

[Claim 3] The Cr-Si film according to claim 1 or 2, wherein the absolute values of TCR in increments of 10°C in the temperature range are each 0 ppm/°C or more and 50 ppm/°C or less.

[Claim 4] The Cr-Si film according to any one of claims 1 to 3, wherein an absolute value of an average TCR in increments of 10°C in the temperature range is 0 ppm/°C or more and 10 ppm/°C or less.

[Claim 5] The Cr-Si film according to any one of claims 1 to 4, wherein the composition range of the film is Cr/(Cr + Si) = 0.3 to 0.5.

[Claim 6] The Cr-Si film according to claim 1, wherein the Cr-Si film has a resistivity of 1.0×10^{-4} Ω·cm or more at 30°C .

[Claim 7] The Cr-Si film according to claim 6, wherein Si - N = 25 to 75 wt%.

[Claim 8] A method for producing the Cr-Si film according to any one of claims 1 to 7, the method comprising forming a film using a sputtering target containing chromium and silicon as a main component

by a sputter method.

[Claim 9] The method for producing the Cr-Si film according to claim 8, further comprising subjecting a Cr-Si film formed by a sputtering method to heat treatment in a non-oxygen atmosphere at 500°C or higher and 800°C or lower.