

DESCRIPTION

HEATING RESISTOR AND MANUFACTURING METHOD THEREOF

Technical Field

The present invention relates to a heating resistor and a method of
5 manufacturing the heating resistor. More particularly, the present invention
relates to a heating resistor which has stable high resistivity which hardly shifts by
heat while having excellent cavitation resistance, thus, is suitable for a thermal
ink-jet printer, and to a method of manufacturing the heating resistor.

Background Art

10 The conventional heating resistors are likely to show unstable resistivity
caused by heat. More precisely, a resistor which has greater resistivity is more
likely to show unstable resistivity. Such the unstable resistivity brings hardness
in controlling the resistor, especially in case of utilizing thermal energy of the
resistor.

15 The conventional heating resistors have usually employed elemental
constitutions of: oxide; nitride; oxide/nitride; oxide/nitride/metal;
oxide/nitride/metal/plus another, and the like. According to those constitutions,
many materials have been proposed. For example, Si-N-Ir-(Ru), Si-N-Ir-(Pt), Si-
N-Ir-Ru-Pt, Si-O-Ir-(Ru), Si-O-Ir-(Pt), Si-O-Ir-Ru-Pt, Si-C-Ir-(Ru), Si-C-Ir-(Pt),
20 Si-C-Ir-Ru-Pt, and the like.

Materials having the above constitutions have not contributed to reduction of
resistivity shifts caused by heat. In other words, many situations requiring
thermal energy of the heating resistors have been intolerant of resistivity shifts of
the conventional heating resistors.

25 On the contrary, thermal ink-jet printers have been used widely, and many of
them employ heating resistors in their print heads. There are side shooter type
head and roof shooter type head which are employed in the thermal ink-jet printers.
The side shooter type head pushes out ink in the direction parallel to a heating
surface of a heating resistor, while the roof shooter type head pushes out ink in the

direction perpendicular to a heating surface of a heating resistor.

FIGS. 1A to 1C are cross sectional views schematically showing a side shooter type head, and FIGS. 1D to 1F are cross sectional views schematically showing a roof shooter type head. As shown in FIG. 1A or 1D, a heating resistor 2 is formed on a silicon substrate 1, and an orifice plate 3 faces the silicon substrate 1. A reference numeral 4 denotes a nozzle. In the side shooter type head, a gap between the silicon substrate 1 and the orifice plate 3 at their side end forms the nozzle 4 as shown in FIG. 1A, while the roof shooter type head has the nozzle 4 which is formed above the heating resistor 2 as shown in FIG. 1D. In both structures, the heating resistor 2 is connected to electrodes (not shown), and a gap between the silicon substrate 1 and the orifice plate 3 forms an ink path 5 to which ink is always supplied.

An ink droplet is pushed out from the print head in accordance with the following steps 1) to 5). 1) When an electrical current representing image data flows through the heating resistor 2, the resistor 2 heats an ink layer to boil it, thus, vapor cores appears above the heating resistor 2 (FIG. 1B or 1E). 2) The vapor cores are gathered into one, thus, a vapor bubble 6 is formed. 3) As the vapor bubble 6 expands, it pushes ink 5-1 through the nozzle 4 to form a droplet 5-2 at the tip of the nozzle 4, and the pressure of the vapor bubble forces the droplet onto the paper (FIG. 1C or 1F). 4) The vapor bubble contracts. 5) The vapor bubble 6 collapses, and the resultant suction pulls fresh ink to stand by for next heating. The above steps 1) to 5) complete within a very short time period.

Effect through the above steps 1) to 3) is caused by film boiling. Film boiling phenomenon usually occurs when a highly heated matter is dipped in liquid (for example, iron quenching), or radically heating a surface of a matter which contacts liquid. The most of the ink-jet printers utilize the latter cause. As a result of the film boiling, suction occurs after bubble collapse. Such the suction is called cavitation.

FIG. 2A is a diagram schematically showing a vapor bubble step by step from

generation to collapse. In this case, the heating resistor 2 is placed in an opened pool having 1 mm depth. It takes 6 microseconds from the bubble generation to collapse. FIG. 2A shows the bubble at every microsecond, and FIG. 2B shows timing of current flow applied to the heating resistor 2.

5 As shown in FIG. 2B, an electrical current flows through the heating resistor 2 for 1 microsecond, thus the heating resistor 2 heats the ink during the first period of 1 microsecond. During next 1 microsecond period, a vapor bubble which will push out an ink droplet appears, and it immediately contracts before the time advance reaches 3 microseconds. Once the bubble starts to contract, the pressure
10 inside the bubble is reduced rapidly and the bubble collapses completely at 6 microseconds. The pressure reduction causes negative pressured cavitation shown by arrows a-1, a-2, and a-3 in FIG. 2A.

The negative pressured cavitation impacts on the heating resistor 2 to pull it up. In case of the above opened pool having 1 mm depth, the force pulling up the
15 heating resistor 2 reaches 1000 ton/cm². In an ink-jet printer, a heating resistor in a print head is an approximately 40 micrometers square, therefore, the impact force will be 16 kg.

The heating resistor is required to have enough resistivity greater than predetermined level. The predetermined level requires the least resistivity for
20 emitting desired thermal energy at a maximum current which is tolerable in a circuit for driving the heating resistor. In a monolithic type print head in which a drive circuit and a heating resistor are placed on the same board, the maximum current for driver's transistor is approximately 100mA. In this case, required resistivity is equal to or greater than 4mΩcm. Generally, such the large
25 resistivity is not available by a metal resistor.

The thermal ink-jet printer requires a heating resistor which satisfies the following conditions: 1) Resistivity — Not typical resistivity that the metal resistor has, that is, large resistivity equal to or greater than 4mΩcm, more preferably, equal to or greater than 5mΩcm. 2) Anti-Heat Stability — Alteration rate of

resistivity by heat is equal to or smaller than $0.05 \text{ }^\circ\text{C}^{-1}$, more preferably, close to $0 \text{ }^\circ\text{C}^{-1}$. 3) Cavitation Resistance — Withstand over 100,000,000 pulses through the open pool test.

As for the resistivity, in a case where a maximum current for driver's transistor is approximately 100mA with electrical power of 1W per pulse, required resistance value may be 100Ω . Most of the heating resistors are metal resistors, therefore, ordinary resistivity is equal to or smaller than $1\text{m}\Omega\text{cm}$.

The thermal ink-jet printer usually employs square heating resistors. If resistor's resistivity is equal to or smaller than $1\text{m}\Omega\text{cm}$, the square heating resistor is required to have its thickness approximately 100 nm in order to emit desired thermal energy. 100 nm thick is too thin to keep resistor's life long.

Material whose constitution is Ta-Si-O or similar one, is known as suitable material for a heating resistor because of its relatively excellent characteristics. However, life of a heating resistor made of such the material does not reach demanded level in case of $4\text{m}\Omega\text{cm}$ resistivity. More precisely, the heating resistor can not withstand 100,000,000 pulses through the opened pool test with water. To make matters worse, alteration rate of resistivity by heat is $0.05 \text{ }^\circ\text{C}^{-1}$ which is still larger than tolerable level.

Under the above conditions, the heating resistor made of Ta-Si-O material require a protection film when the resistor is put in use of an ink-jet printer. The protection film protects the heating resistor from being eroded by ink and from being damaged by the cavitation. Covering the heating resistor with the protection film of approximately 1 micrometer thick impedes thermal energy emitted by the resistor. Since such the output loss requires more power, the conventional Ta-Si-O heating resistor hardly respond to demands for power saving.

Disclosure of Invention

It is an object of the present invention to provide a heating resistor having high resistivity, low rate of alteration by heat, and excellent cavity withstand, thus

suitable for a thermal ink-jet printer.

The above object is achieved by a heating resistor which emits heat by applying electric current thereto,

said heating resistor (12) comprises at least tantalum (Ta), silicon (Si), oxygen (O), and nitrogen (N) as component elements.

Thus structured heating resistor is suitable for a thermal ink-jet printer because it shows stabilized high resistivity like a non-metallic material but small resistivity alteration by heat, while having excellent cavitation resistance like a metallic material.

10 In the heating resistor, mol% of nitrogen (M2) may be $5\text{mol}\% \leq M2 \leq 25\text{mol}\%$. In this case, mole ratio Si/Ta may be $0.35 < \text{Si/Ta} < 0.80$, further, mol% of oxygen (M1) may be $25\text{mol}\% \leq M1 \leq 45\text{mol}\%$.

Of the above settings, only mole ratio Si/Ta of $0.35 < \text{Si/Ta} < 0.80$ may be selected, or only oxygen mol% (M1) of $25\text{mol}\% \leq M1 \leq 45\text{mol}\%$ may be selected.

15 The heating resistor may comprise amorphous structure, wherein broad peak angle of X-ray diffraction strength appearing in X-ray diffraction is equal to or smaller than 37.5 degrees, and resistivity is equal to or greater than $4\text{m}\Omega\text{cm}$.

Moreover, the heating resistor may comprise amorphous structure, wherein light absorption coefficient at light energy of 0.5 to 1 eV is 70,000/cm or less, and
20 resistivity is equal to or greater than $4\text{m}\Omega\text{cm}$.

The heating resistor (12) may be employed in a print head of an ink-jet printer. In this case, the heating resistor (12) may directly contacts ink, and generates a bubble in the ink. Thus, a print head of a thermal ink-jet printer having improved energy efficiency for better droplet output and excellent cavitation resistance.

25 It is another object of the present invention to provide a method of manufacturing a heating resistor having high resistivity, low rate of alteration by heat, and excellent cavity withstand, thus suitable for a thermal ink-jet printer.

The above object is achieved by a method of manufacturing a heating resistor (12) which emit heat by applying electric current thereto, comprises the steps of:

forming a thin film made of Ta-Si-O-N (12) on a substrate (11); and
forming the heating resistor (12) by annealing said Ta-Si-O-N film.

In the above method, the annealing may be carried out under the air. In this case, the annealing step can be done easily.

- 5 In the above method, the annealing may be carried out under inert gas. In this case, an electrode film or the like is prevented from being oxidized during annealing, thus, problems caused by the oxidization does not occur.

In a case where heating resistor is employed in a print head of a thermal ink-jet printer, temperature during the annealing may be 350 to 600 degrees Celsius.

- 10 In a case where the print head of the thermal ink-jet printer is a monolithic head in which a head and a drive circuit are mounted on the same silicon substrate, temperature during the annealing may be 350 to 450 degrees Celsius.

In the above method, the annealing may be carried out for 10 to 30 minutes.

- The Ta-Si-O-N film may have a protection film (21) thereon. In this case,
15 the Ta-Si-O-N film (12) is annealed while it has the protection film (21) thereon, and the annealing may be carried out under the air. Thus, the electrode film or the like is prevented from being oxidized.

Brief Description of Drawings

- These objects and other objects and advantages of the present invention will
20 become more apparent upon reading of the following detailed description and the accompanying drawings in which:

FIGS. 1A, 1B, and 1C are diagrams each schematically showing ink ejection step by step for explaining principle of operations in a conventional side shooter type print head;

- 25 FIGS. 1D, 1E, and 1F are diagrams each schematically showing ink ejection step by step for explaining principle of operations in a conventional roof shooter type print head;

FIG. 2A is a diagram schematically showing process of bubble growth at every 1 microsecond observed through opened pool test, and FIG. 2B is a diagram

showing timing of current flow through a heating resistor during the opened pool test;

FIG. 3 is a cross sectional view schematically showing a heating area in a print head of a thermal ink-jet printer and peripheral structure according to one embodiment of the present invention;

FIG. 4 is a table in which constitutions and resistivities of typical three samples for the heating resistor;

FIG. 5 is a graph, for explaining grounds of the present invention, showing relationship between resistivity and peak angle which appears after X-ray diffraction for Ta-Si-O films and Ta-Si-Al-O films having different constitution ratios;

FIG. 6 is a graph showing results of X-ray diffraction for one of Ta-Si-O-N materials;

FIG. 7 is a graph showing relationship between peak angle after X-ray diffraction and resistivity for Ta-Si-O-N material, and Ta-Si-O and Ta-Si-Al-O materials shown in FIG. 5;

FIG. 8 is a graph showing relationship of resistivity and temperature for the Ta-Si-O-N film for comparison with the conventional technique;

FIG. 9 is a graph showing light absorption characteristics of the Ta-Si-O-N film formed on a silicon substrate;

FIG. 10 is a graph showing results of opened pool test using multiple heating resistors made of sample No. 1 shown in FIG. 4;

FIG. 11 is a graph showing results of opened pool test using multiple heating resistors made of sample No. 2 shown in FIG. 4;

FIG. 12 is a table listing results of closed pool test using sample No. 2 and results of the opened pool test;

FIG. 13 is a table listing 11 samples of the Ta-Si-O-N film having different constitution ratios including samples Nos. 1 to 3 shown in FIG. 4 and additional samples Nos. 4 to 11;

FIG. 14 is a graph showing relationship between peak angle and resistivity of samples Nos. 1 to 11 after adding results of samples Nos. 4 to 11 to the graph shown in FIG. 7;

FIG. 15 is a graph showing resistivity alterations of an annealed Ta-Si-O-N film and a non-annealed one;

FIG. 16 is a graph showing results of the SST (Step-up Stress Test) for the annealed heating resistor and the non-annealed heating resistor;

FIG. 17 is a cross sectional view schematically showing the structure near a heating area in a print head of a thermal ink-jet printer according to one embodiment of the present invention;

FIGS. 18A, 18B and 18C are cross sectional views for explaining manufacturing process of the printer head of the thermal ink-jet printer shown in FIG. 17 step by step;

FIG. 19 is a graph showing relationships each between annealing temperature and increase rate of sheet resistivity after annealing under four different conditions; and

FIG. 20 is a graph showing relationships each between process time for annealing and relative resistivity after annealing under four different conditions.

Best Mode for Carrying Out the Invention

A preferred embodiment of the present invention will now be described with reference to accompanying drawings.

FIG. 3 is a cross sectional view schematically showing a print head, especially the structure of a heating area and its peripherals. A print head shown in FIG. 3 is a so-called roof shooter type head. Unillustrated component in the print head is an oxide layer (SiO_2) having the thickness of 1 to 2 micrometers which is formed on a surface of a chip substrate.

A reference numeral 12 denotes a heating resistor film made of at least 4 component elements, Ta (tantalum), Si (silicon), O (oxygen), and N (nitrogen), which is formed on the oxide layer by a thin film forming technique. The heating

resistor film 12 is patterned by photolithography technique to have striped shape. Prepared electrode film made of Au or the like also has striped pieces. Pieces of striped electrode film are deposited onto the heating resistor film 12 so that a pair of the electrode pieces cover ends of a piece of heating resistor film 12, thus, center of each piece of the heating resistor film 12 is exposed. At the electrode film formation, a barrier layer made of Ti-W or the like is formed so that the barrier layer intervenes between the electrode film and the heating resistor film 12. Exposed areas of the heating resistor film 12, that is, areas being not covered with the electrode film act as heating areas 13. In each pair of the electrode pieces, one electrode piece will act as individual electrodes 14 while the other one will act as common electrodes 15.

After forming the heating areas 13, an organic material such as polyimide is coated on the chip substrate 11 as a to-be-wall layer so as to have the thickness of approximately 20 micrometers. The to-be-wall layer is patterned by the photolithography technique so that the layer remains on the individual electrodes 14, and the chip substrate 11 is subjected to curing by which the chip substrate 11 is exposed to heat whose temperature is 300-400 degrees Celsius for 30-60 minutes. Thus, walls 16 made of photosensitive polyimide whose height is approximately 10 micrometers are formed on the individual electrodes 14.

After forming the heat areas 13 and walls 16, an orifice plate 17 is deposited on the chip substrate 11 as a top layer. Then, the orifice plate 17 is etched (dry etching) with using a metal mask (not shown) to form nozzles 18 in the orifice plate 17 just above the heating areas 13. Intervals among the nozzles 18 are minute, for example, approximately 40 micrometers. Since the orifice plate 17 is formed on the walls 16, the orifice plate 17 and the common electrodes 15 are spaced from each other. The spaces each having the height of 10 micrometers (which is the same as the height of the walls 16) work as ink paths 19. Ink is supplied to spaces above the heating areas 13 via the ink paths 19.

As shown in FIG. 3, the heating areas 13 are exposed, in other words, they

have no protection layer or the like thereon. The protection layer has been employed in this type of print head usually, and has the thickness of no less than 1 micrometer. No protection layer structure greatly improves energy efficiency for ink emission.

- 5 As aforementioned, the heating resistor film 12 has component elements at least Ta, Si, O, and N. Preferable ranges of element constitutions are as follows. Si/Ta mole ratio: $0.35 < \text{Si/Ta} < 0.80$, more preferably, $0.35 < \text{Si/Ta} < 0.45$. M1 (mol% of O): $25\text{mol}\% \leq \text{M1} \leq 45\text{mol}\%$. M2 (mol% of N): $5\text{mol}\% \leq \text{M2} \leq 25\text{mol}\%$.

The heating resistor film 12 has the following properties: amorphous structure; angle at peak of X-ray diffraction strength is equal to or less than 37.5 degrees; resistivity is equal to or greater than $4\text{m}\Omega\text{cm}$; and light absorbency coefficient at 0.5-1eV is less than 70,000/cm.

The heating resistor according to the present invention features four-element constitution including Ta, Si, O, and N. This structure is advanced structure based on conventional constitution Ta-Si-O which has showed relatively excellent performance for a heating resistor. The above four-element constitution is a result after testing many prototypes with various constitutions of Ta-Si-O plus other elements through experiments.

FIG. 4 shows a table indicating constitutions of typical 3 samples having the four-element constitution which are trial productions for testing. As shown in FIG. 4, constitution elements of the samples are Ta, Si, O, and N. The table shows mol% of the elements for each, Si/Ta mole ratio, mol% of O+N, and resistivity ($\text{m}\Omega\text{cm}$).

Since the results shown in the table have tolerance margins of errors, sum of mol% of four elements is not just 100%. That is, total mol% of the samples are as follows. sample 1: 100.1%, sample 2: 99.7%, and sample 3: 100.6%.

FIG. 5 is a graph for explaining merits of the four-element heating resistor featured in the present invention. The graph shows characteristic lines each indicating relationship between peak angles 2θ after X-ray diffraction and

resistivities of 8 samples. The samples includes 6 Ta-Si-O constitution materials and 2 Ta-Si-Al-O constitution materials each having different constitutional ratio. θ represents reflection angle of Bragg reflection, and the peak angle means angle of broad peak of X-ray diffraction strength. In the graph, a horizontal axis represents the peak angle 2θ (deg), while a vertical axis represents resistivity ($m\Omega cm$) in logarithmic scale.

A line "a" represents characteristics of 6 Ta-Si-O constitution samples, while a line "b" represents characteristics of 2 Ta-Si-Al-O constitution samples. It is obvious from not only the line "a" but the line "b" that there is a correlation between peak angle 2θ and the resistivity. Through the experiment, peak angle 2θ is likely to decrease as oxygen amount increase. The inventors studied this phenomenon as follows.

The aforementioned broad peak is typically shown in materials having the amorphous structure. Appearance of such the broad peak is reflection of structure factor (reciprocal space) which represents order of the closest atoms. For example, structure factor of three-element (A, B, and C) compound as a whole is the sum of 6 structure factors of A-A, A-B, B-B, A-C, B-C, and C-C. Fourier transform of the structure factor of the compound results average atomic order therein.

Accordingly, the peak angle reflects the average atomic order. That is, peak angle 2θ correlates with the resistivity as shown in FIG. 5. According to this fact and the relationship between oxygen amount and peak angle 2θ , the inventors had come to have inference that the peak angle may reflect average interatomic distance and configuration of positive ions and negative ions (oxygen) (such as Ta-O, Si-O, and Al-O). The inference further suggests that average interatomic distance of Ta-Ta and Ta-Si also depends on oxygen density, thus, the peak angle also reflects the average interatomic distance of Ta-Ta and Ta-Si.

The inference consistent with the result shown in FIG. 5 that points representing Ta-Si-Al-O samples are scattered as resistivity decrease along the

characteristic line "a" (lower right in the graph). This fact is provable by a fact that lower the resistivity becomes, greater influences caused by orders among positive ions becomes because the number of negative ions decreases as the resistivity decreases.

5 Accordingly, the peak angle resulted from the X-ray diffraction reflects connection between the closest atoms. This fact suggests that the peak angle may reflect strength and cavitation resistant of a heating resistor. Moreover, the resistivity may reflect band structure of the samples, that is, connection among atoms.

10 The examiners also paid attention to the fact that the characteristic lines "a" and "b" are not parallel to each other. More precisely, the characteristic line "b" (Ta-Si-Al-O) shows greater resistivity (at upper in the graph) than the characteristic line "a" (Ta-Si-O) as peak angle 2θ increase (near right end of the graph).

15 This fact may be caused because valence of Al is smaller than that of Si and Ta. In this case, Si is four-valence atom, Ta is five-valence atom, and Al is three-valence atom. Based on this inference, the examiners focused on elements which alter valence. In fact, it had been observed that the resistivity increases as Si increase in Ta-Si-O material. This fact suggests that Si-rich material tends to
20 show greater resistivity as the peak angle increase.

The examiners regarded constitutions Ta-Si-O and Ta-Si-Al-O as combinations of positive ions and negative ions, that is, (Ta-Si)-O and (Ta-Si-Al)-O, and had the following inference.

Further, if atom in a material has smaller valence, it shows higher resistivity.
25 Moreover, since electrons in a material which shows high resistivity in a peak angle range equal to or less than 37.5 deg. (untypical range in a metal resistor) are localized, chemical connection in the material may be strong. This fact suggests that the material has improved cavitation resistant.

The examiners had also observed that alteration rate of resistivity by heat

(temperature coefficient) in a material which shows smaller peak angle is small.

According to the above facts, a material which shows high resistivity and small peak angle is suitable for a heating resistor of the present invention. A typical heating resistor made of metal has small heat alteration rate of resistivity, however, it never shows high resistivity suitable for the heating resistor. Then, the examiners have drawn an inference that non-metal material may shows smaller peak angle and higher resistivity.

Further, a preferable material should have another negative ion element ((Ta-Si)-(O-β)), because it is obvious from the characteristic line "b" ((Ta-Si-Al)-O) that it is difficult to increase resistivity up to $4\text{m}\Omega\text{cm}$ or more when peak angle 2θ is small in case of (Ta-Si-α)-O material. If nitrogen whose valence is minus 3 as negative ion element, the material is likely to show high resistivity because valence of oxygen is minus 2. It suggests that the material will show resistivity equal to or greater than $4\text{m}\Omega\text{cm}$ when peak angle 2θ is equal to or smaller than 37.5° (untypical range in metal material). Based on the above inference, the examiners made a film made of Ta-Si-O-N constitution material by DC sputtering under mixed atmosphere of Ar, O, and N to sputter a striped target of Ta and Si.

The sputtering was carried out under the following conditions. Ultimate Pressure: $0.5 \times 1.33 \times 10^{-4}\text{Pa}$, Sputtering Power: 1kW, and Film Forming Rate: 2.4nm/min, with an Si substrate for analysis and another Si substrate on which 1-micrometer SiO_2 layer for pulse resistant test, in a same chamber.

After annealing thus formed Ta-Si-O-N film, a stabilized heating resistor whose properties of resistivity, heat alteration rate of resistivity, and the like are stable, that is, those are not varied as time goes by.

FIG. 6 is a graph showing results of X-ray diffraction analysis for the Ta-Si-O-N film (sample No. 3 in FIG. 4). Pattern of X-ray diffraction strength shown by the graph has a single broad peak which represents that the film has amorphous structure. Unit of the X-ray diffraction strength is arbitrary unit.

FIG. 7 is a graph showing relationship between peak angle position and

resistivity for three samples of the Ta-Si-O-N film having different constitution ratio shown in FIG. 4. The graph also shows the characteristic line "a" (Ta-Si-O) and the characteristic line "b" (Ta-Si-Al-O) as reference. It is obvious from the graph that the three materials concerned show results in an area where the peak angle is equal to or smaller than 37.5 deg while the resistivity is equal to or greater than 4mΩcm. The result shows that those materials are suitable for a heating resistor in a thermal ink-jet printer.

The constitution ratios of the three samples shown in FIG. 4 are resulted by carrying out RBS (Rutherford Backscattering Spectrometry) to analyze a heating resistor film on a Si substrate. Since the RBD hardly detect nitrogen which is light, amount of N in the sample Nos. 1 and 2 which have relatively less nitrogen were detected by ESCA (Electron Spectroscopy for Chemical Analysis) which is one of photoelectron spectroscopy.

FIG. 8 is a graph showing relationship between resistivity of the heating resistor (Ta-Si-O-N) and temperature of the sample No. 2 shown in FIG. 4. The graph also shows the relationship of conventional two materials (Ta-Si-O). In the graph, a characteristic line "d" represents the relationship of the sample No. 2, while a characteristic line "e" represents results of a conventional Ta-Si-O heating resistor whose resistivity under a room temperature is 4mΩcm, and a characteristic line "f" represents results of another conventional Ta-Si-O heating resistor whose resistivity under a room temperature is 2mΩcm. A horizontal axis of the graph represents temperature (degrees Celsius) and a vertical axis thereof represents ratio of resistivity under a room temperature "R (room temperature)" to altered resistivity "R (T)" under a temperature T.

Those materials are formed on silicon substrates in the same chamber for measurement. The materials are patterned as well as the aforementioned case of opened pool test. Each heating resistor film of Ta-Si-O-N is a 40 micrometers square.

The resistivity is obtained by measuring a voltage applied to the heating

resistor through which a current flows. The voltage is measured by a digital voltmeter. Temperature alters as the current alters. The temperature is measured by an infrared emission thermometer which can measure temperature on a minute area. As shown in FIG. 8, alteration rate of resistivity by heat of the Ta-Si-O-N heating resistor represented by the characteristic line "d" is 10% at 400 degrees Celsius (0.025% / a degree Celsius), while the resistivity is equal to or greater than $5\text{m}\Omega\text{cm}$. On the contrary, resistivity alteration rates by heat of the conventional materials represented by the characteristic lines "e" and "f" are twice as large as or more than the characteristic line "d".

FIG. 9 is a graph showing light absorption characteristics of the Ta-Si-O-N heating resistor film formed on the silicon substrate. The inventors focused on the light absorption characteristics to observe the characteristics of the Ta-Si-O-N heating resistor film from different view point. The graph shows the light absorption coefficient, and the resultant coefficient was obtained based on light transmittance of a sample whose constitution ratio is the same as that of the sample No. 2 shown in FIG. 4 and having arbitrary thickness.

A horizontal axis of the graph shown in FIG. 9 represents light energy (eV), while a vertical axis thereof represents light absorption coefficient (cm^{-1}). According to the graph, the resultant absorption coefficients in energy range of 0.5 to 1 eV are small (equal to or smaller than $70,000/\text{cm}$), while the absorption coefficient gradually increase in a higher energy area which shows 1 eV or more energy. It is obvious from FIG. 9 that the resultant absorption coefficients are not close to 0, and there is no obvious optical gap.

Behavior of the shown light absorption characteristics as a whole suggests that there is a band gap. That is, the heating resistor made of sample No. 2 shown in FIG. 4 is similar to a degenerate semiconductor because of the optical characteristics and small temperature coefficient (resistivity alteration rate by heat is equal to or smaller than 0.025 %/degree Celsius). In other words, the heating resistor is similar to a degenerate semiconductor which has energy distribution of

carrier (free electron or positive hole) is degenerated Fermi distribution.

Then, an opened water pool test was carried out for evaluating cavitation resistance. For the test, a Ta-Si-O-N material formed on an oxidized Si substrate in the same chamber where sample No. 1 shown in FIG. 4 was formed, was
5 prepared, and a W-Ti film and an Au film for wiring were formed on the material and patterned out.

The prepared heating resistor for the opened pool test is a 25 micrometers square with the thickness of 480 micrometers. Pulses whose frequency is 10kHz while having 1 micrometer second pulse width were applied to the heating resistor.
10 The frequency and pulse width were determined based on ink output performance of an ink-jet printer head which employs a prototype heating resistor produced under the same conditions.

FIG. 10 is a graph showing results of the opened water pool test of the sample which was formed in the same chamber where sample No. 1 shown in FIG. 4 was
15 formed. An horizontal axis of the graph shown in FIG. 10 represents the number of applied pulses, while a vertical axis thereof represents resistance value (Ω). As shown in FIG. 10, none of 9 heating elements (ch00 to ch64) shows broken line after applying pulses 100,000,000 times, that is, excellent result was obtained. Moreover, no significant damage was observed by an electron microscope after the
20 test.

FIG. 11 is a graph showing results of another opened water pool test of a sample which was formed in the same chamber where sample No. 2 shown in FIG. 4 was formed. As well as FIG. 10, a horizontal axis of the graph shown in FIG. 11 represents the number of applied pulses, while a vertical axis thereof represents
25 resistance value (Ω). FIG. 11 shows a case where the pulses were applied to the sample until lines are broken. Of nine heating elements (ch00 to ch64), first line break was found after applying pulses 200,000,000 times, as shown in FIG. 11.

It has been known that the opened pool test is one of the hardest tests, that is, it is almost destructive testing. Ability of the heating resistor for withstanding

over 100,000,000 pulses means that the heating resistor has permanent level durability for an ink-jet printer.

As shown in FIG. 4, resistivity of samples Nos. 1 and 2 having excellent cavitation resistance is $5\text{m}\Omega\text{cm}$ or more. This is far above the average level 5 required for a heating resistor in an ink-jet printer head.

The inventors produced another prototype head to prove their inference firmly. The prototype is made of a material in the same chamber of sample No. 2. Nozzles of the prototype head are formed in an orifice plate which is formed on walls. A test to observe deterioration of a heating resistor made of sample No. 2 10 in view of cavitation resistance by letting the head output water and ink. The test is called closed pool test in contrast with the opened pool test.

FIG. 12 is a table showing results of closed pool test and opened pool test (sample No. 2; using water). Regardless of no protection film structure, the heating resistor made of sample No. 2 withstands 200,000,000 pulses through the 15 opened pool test, and 1,000,000,000 pulses through the closed pool test. Those results achieve the goals (100,000,000 pulses for the opened pool test; 1,000,000,000 pulses for the closed pool test).

In case of using ink (black ink), applied pulses are limited to approximately 300,000,000 times because of deterioration of materials other than the heating 20 resistor. However, no deterioration was found on the heating resistor immediately after the test.

Thus, it is proved that the heating resistor film having constitution of Ta-Si-O-N shows excellent characteristics for an ink-jet printer head. The inventors further made several resistor films of Ta-Si-O-N whose constitution ratios are 25 differed from each other to find preferable constitution ratio.

FIG. 13 is a table in which characteristic elements of constitution ratio, resistivity, opened pool test result, and peak angle each for samples Nos. 1 to 11 (Nos. 1 to 3 are shown in FIG. 4) are listed. Constitution ratios of the additional materials (Nos. 4 to 11) are differed from each other based on inventors'

experiences through the above experiments.

Of 11 materials, material Nos. 7, 10 and 11 failed the pulse resistance test. Since they could not withstand 100,000,000 pulses, they are not suitable for a heating resistor in a thermal ink-jet printer. Some of the characteristic elements 5 mol% of O, mol% of N, and Si/Ta in each of the failed materials show extremely large or small values (hatched sections in the table) rather than other materials which passed the pulse resistance test.

Preferable value ranges for excellent characteristics as a heating resistor were determined as follows based on the materials which passed the pulse resistance test 10 and other experiments. mol% of O (M1): $25\text{mol}\% \leq M1 \leq 45\text{mol}\%$, mol% of N (M2): $5\text{mol}\% \leq M2 \leq 25\text{mol}\%$, and mole ratio Si/Ta: $0.35 < \text{Si/Ta} < 0.80$.

FIG. 14 is a diagram which is prepared based on the graph shown in FIG. 7 (relationship between peak angle and resistivity) but further shows results of the characteristics in the materials Nos. 4 to 11. In the graph, black dots represent 15 results of the materials which passed the pulse resistance test, while white dots represent the materials which failed the pulse resistance test.

The aforementioned description related to FIGS. 5 and 7 indicated that the area restricted by the peak angle equal to or smaller than 37.5 deg and by the resistivity equal to or greater than $4\text{m}\Omega\text{cm}$ is preferable one for a heating resistor. 20 However, FIG. 14 teaches that all Ta-Si-O-N materials (Nos. 1 to 11) are in the range. That is, even the materials Nos. 7, 10, and 11 which failed the pulse resistance test are in the range. Therefore, the range proposed as the preferable one is not suitable for evaluating durability such as cavitation resistance or the like of the heating resistor in a thermal ink-jet printer.

25 The resistivity of the Ta-Si-O-N heating resistor film is likely to change as time goes by. Such the resistivity alteration may affect on reliability and design of a product using the heating resistor. In case of the Ta-Si-O-N made by sputtering, however, it has been known based on experiments that annealing stabilizes resistor characteristics (such as resistivity, and alteration rate of

resistivity by heat).

Accordingly, annealing is a significant step for produce stable Ta-Si-O-N resistor film. Process for forming a heating resistor of Ta-Si-O-N film with annealing will now be described in detail.

- 5 Sputtering is carried out by a sputtering apparatus under the following conditions. Target: Ta plate including predetermined amount of Si (for example, Ta:Si = 3:1), Pressure: equal to or lower than 1.33×10^{-4} Pa, Process Gas: predetermined amount of Ar, Substrate Temperature: approx. 200 degrees Celsius, and Layer Forming Rate: approx. 2 nm/sec.
- 10 A Ta-Si-O-N film whose thickness is 480 nm is formed on the Si substrate which is thermally oxidized by the above described sputtering. As aforementioned, thus formed material has the amorphous structure which is proved by X-ray diffraction. The material will have varied resistivity as time goes by unless it is annealed.
- 15 FIG. 15 is a graph showing characteristic alterations between an annealed film and a non-annealed film. Used material for comparison was sample No. 4 shown in FIG. 13 whose constitution ratio is: 42.0% of Ta, 16.0% of Si, 30.0% of O, and 12.0% of N. In this case, the annealing was carried out under atmosphere at 400 degrees Celsius.
- 20 A horizontal axis of the graph represents time period in logarithmic scale in order to show long period, while a vertical axis represents resistivity alteration. The resistivity alteration on the vertical axis shows relative alteration. In this case, 100 represents initial resistivity immediately after layer formation (at 1 on the logarithmic scale for easy comprehension) as a reference value. In the graph,
- 25 black circle dots (line "h") represent results of the non-annealed material, while black square dots (line "g") represent results of the annealed material.
- As indicated by the line "h", the resistivity of the non-annealed material increases as time goes by. On the contrary, the resistivity of the annealed material shows 20 to 30% increase caused by the annealing, however, the line "g"

shows constant resistivity regardless of time lapse.

The annealed resistor film was further subjected to the Auger electron spectroscopy test to find an oxidized film or oxygen distribution. The test reveals that the annealing brings no oxidized film and oxygen distribution, because only a native oxidized film having 3 to 5 nm thick (which is 0.1% of the film thickness) was found through the test. This fact suggests that cause of the increase of resistivity at annealing is not oxidization.

To investigate characteristic differences between the annealed film and non-annealed film, the step-up stress test (SST) in an opened pool was carried out.

10 Materials to be used for the SST were formed under almost the same conditions for forming sample No. 4 shown in FIG. 13.

FIG. 16 is a graph showing results of the SST of the annealed and non-annealed materials. A horizontal axis of the graph represents energy (μJ) of applied pulses (2 μsec . pulse at 10kHz), while a vertical axis thereof represents alteration rate of resistivity (%). In this case, the annealed film has the thickness of 360 nm, while the thickness of the non-annealed film is 700 nm. Both annealed and non-annealed films are 25 micrometers square. In the graph, black circle dots along a line "i" represent results of annealed film, while black square dots along a line "j" represent results of the non-annealed film.

20 The range of the energy of applied pulse was set to approximately 1.2 μJ to 5 μJ . 1.2 μJ is minimum level required for forming a bubble which pushes out ink droplet, and 5 μJ is a point which causes the material (heating resistor film) to discolor, that is, the film no longer withstands the stress. Initial resistivity was set as a reference resistivity for indicating the alteration ratio of the resistivity. A thicker film is generally stronger while the other conditions are the same.

However, the non-annealed film which is thicker shows larger alteration rate of resistivity at a point where the material discolors.

A range between broken lines k and m (2 μJ to 3 μJ) represents a practical range for ink ejection. In the range, the resistivity alteration range of the

annealed material (the line "i") is stable, while the resistivity alteration range of the non-annealed material (the line "j") is unstable (once decrease and increase little).

According to not only the alteration as time goes by shown in FIG. 15, but also to the results which are applicable to practical use, the annealing to a formed Ta-Si-O-N film is very effective factor for producing a film having stable characteristics.

The above annealed heating resistor film were formed by the following steps. Carrying out sputtering (Target: Ta plate including Si, Vacuum Pressure: $\leq 1.33 \times 10^{-4}$ Pa, Substrate Temperature: 200 degrees Celsius, Process Gas: Ar, Layer Forming Rate: 2 nm/sec.), forming an electrode layer, patterning the electrode layer and the heating resistors, then annealing the heating resistors (under atmosphere at 400 degrees Celsius for 10 minutes).

Electrodes for driving the heating resistors according to the above embodiment of the present invention have dual layer structure (not shown in FIG. 3) of a W-Ti film and an Au film. Since the electrode layer are formed on the heating resistor film, the electrode layer should contact the heating resistor film well. However, the Au film, which is suitable for electrode, has hardness to adhere to Ta-Si-O-N. The W-Ti film of the electrode layer is used as a base film to interconnect the Au film and the resistor film because the W-Ti film adhere to both Au and Ta-Si-O-N well.

In a state where the electrode is exposed to ink, electrolysis caused by a short-circuit current may occur in the ink because the ink is weakly electrolyte. The electrolysis may form extra bubbles which block the ink flow.

In order to avoid the electrolysis, the electrodes should be covered with an insulation film. An oxide insulation film such as Ta-Si-O is preferable one.

FIG. 17 is a diagram showing the insulation film structure according to another embodiment of the present invention. In this embodiment, the heating area 13 of the heating resistor 12 is also covered with the insulation film. As

aforementioned, the Ta-Si-O-N heating resistor film without a protection film shows excellent cavitation resistance, however, the covered structure shown in FIG. 17 is preferable in a case where more cavitation resistance is required rather than energy efficiency.

5 As shown in FIG. 17, the heating area 13, the individual electrode 14, and the common electrode 15 shown in FIG. 3 are covered with a protection film 21 made of Ti-Si-O. FIGS. 18A to 18C are cross sectional views for explaining process of forming the heating element shown in FIG. 17 step by step. FIGS. 18A to 18C shows the structure of the electrodes (individual electrode 14 and common
10 electrode 15) in detail.

As shown in FIG. 18B, the electrode has triple layer structure including a lower adherence film 22 of W-Ti, an electrode film 23 of Au, and an upper adherence film 24 of W-Ti. Thus structured electrode and the heating area 13 are covered with the insulation protect film 21 made of Ta-Si-O material having
15 excellent cavitation resistance.

The upper adherence film 24, which adheres both Au and Ta-Si-O, firmly interconnects the Au electrode film 23 and the Ta-Si-O protection film 21. Thus, the heating element is insulated from the ink.

Steps of forming such the heating element on which the insulation protect
20 film is formed will now be described with reference to FIGS. 18A to 18C.

First, the lower adherence film 22, the electrode film 23, and the upper adherence film 24 are deposited onto the heating resistor film 12 which has been deposited on the chip substrate 11 (FIG. 18A). Then, patterning the lower adherence film 22, the electrode film 23, and the upper adherence film 24 to form
25 the heating area 13, the individual electrode 14, and the common electrode 15 (FIG. 18B). Further patterning the heating resistor film 12 to form the heating element.

The next step should be annealing, however, annealing the heating resistor film 12 under atmosphere while the upper adherence film 24 of W-Ti contacts the electrode film 23 brings an oxidized layer on the upper adherence film 24. More

precisely, oxygen in the air becomes radical atoms caused by high temperature during the annealing under the above conditions. The radical atoms oxidize surface of the upper adherence film 24. Since it is difficult to adhere thus formed oxidized layer to the Ta-Si-O protection film 21, the W-Ti upper adherence film 24 does not function for interconnecting the protection film 21 and the electrode film 23.

The following condition sets for annealing are prepared to avoid oxidized layer formation.

First one is annealing under inert gas in order to avoid generation of radical oxygen. The inert gas is a generic name representing a low reactive gas such as 0 group elements He, Ar, Kr, Xe, and Rn (rare gas), and N₂ gas. In this embodiment, N₂ gas and Ar gas were used.

Steps and detailed conditions are as follows.

- (1) Forming a Ta-Si-O-N heating resistor film.
- 15 (2) Forming a lower adherence film (W-Ti).
- (3) Forming an electrode film (Au).
- (4) Forming an upper adherence film (W-Ti).
- (5) Patterning the electrode layer (W-Ti, Au, W-Ti).
- (6) Patterning the heating resistor film.
- 20 (7) Annealing the heating resistor film.

Atmosphere: N₂ gas (inert gas)

Temperature: 350 to 450 degrees Celsius

Process Period: 10 to 30 minutes

- (8) Forming an oxide insulation film (Ta-Si-O).
- 25 (9) Patterning the oxide insulation film (Ta-Si-O).

According to the above process, the upper adherence film 24 is not oxidized because the annealing is carried out under N₂ gas.

Since the W-Ti upper adherence film 24 is not oxidized, the Ta-Si-O oxide insulation film 21 formed on the upper adherence film 24 tightly, thus, firm

connection between the Ta-Si-O insulation film 21 and the Au electrode film 23 is established.

The same steps are applicable to a case where the annealing is carried out under Ar gas.

5 And another one is annealing in a vacuumed chamber. In this case, the chamber is a sputtering chamber used for sputtering, therefore, the annealing is carried out successively after the heating resistor was formed by sputtering. The annealing in the vacuumed chamber is realized by radiation heat. The above method prevents the radical oxygen from contacting the upper adherence film 24.

10 The annealing may be carried out after forming the Ta-Si-O oxide insulation film in order to prevent the radical oxygen from contacting the upper adherence film 24. In this case, the annealing can be done under atmosphere (air).

Steps and conditions for this method are as follows.

- (1) Forming a Ta-Si-O-N heating resistor film.
- 15 (2) Forming a lower adherence film (W-Ti).
- (3) Forming an electrode film (Au).
- (4) Forming an upper adherence film (W-Ti).
- (5) Patterning the electrode layer (W-Ti, Au, W-Ti).
- (6) Patterning the heating resistor film.
- 20 (7) Forming an oxide insulation film (Ta-Si-O).
- (8) Patterning the oxide insulation film (Ta-Si-O).
- (9) Annealing the heating resistor film.

Atmosphere: Air (atmosphere)

Temperature: 350 to 450 degrees Celsius

25 Process Period: 10 to 30 minutes

FIG. 19 is a graph showing resistivity increase rates of heating resistor films which are annealed but under different atmosphere conditions (atmosphere (the air) indicated by black circles, N₂ gas indicated by black triangles, Ar gas indicated by white triangles, the air after the Ta-Si-O oxide insulation film was formed and

patterned (hereinafter, referred to as "the air with protection film) indicated by crossings). A horizontal axis of the graph represents temperature for annealing ($^{\circ}\text{C}$), while a vertical axis represents sheet resistivity increase rate of the heating resistor film. In this case, process time for the annealing is 10 minutes.

- 5 As shown in FIG. 19, the increase rates of sheet resistivity increase linearly in a temperature range of 200 to 400 degrees Celsius regardless of the atmosphere conditions. Then, the increase rates decrease gently after the temperature exceeds 400 degrees Celsius. Even the increase rate decreases, resistivity itself continuously increases. The results reveal that resistivity stabilizing effect
10 caused by annealing depends only on heat not atmosphere conditions.

For the thermal ink-jet printer usage, the heating resistor should be annealed at least at 350 degrees Celsius, because the heating resistor emits heat equal to or greater than 300 degrees Celsius when it is driven in the printer. In other words, effect brought by the annealing is not shown if the resistor was annealed at equal
15 to or smaller than 300 degrees Celsius. Higher the annealing temperature becomes, smaller the resistivity alteration rate is obtained at the temperature is equal to or greater than 400 degrees Celsius. This fact is obvious from FIG. 19 in which the increase rates are getting smaller when the temperature is equal to or greater than 400 degrees Celsius. However, it has been known that annealing
20 temperature which is greater than 600 degrees Celsius deteriorates cavitation resistance. In case of monolithic structure where the heating resistor and its driver circuit are mounted on the same silicon substrate, maximum annealing temperature is limited to 450 degrees Celsius because "400 degrees Celsius for 1 hour" is a limit for a diffusion layer of an LSI on the silicon substrate. Therefore,
25 a temperature range for annealing the heating resistor to be used in the monolithic thermal ink-jet printer should be 350 to 450 degrees Celsius.

FIG. 20 is a graph whose horizontal axis represents annealing time (min.) while a vertical axis represents relative resistivity where 100 indicates initial resistivity, to show relationship between annealing time and relative resistivity of

the annealed resistor films under difference atmosphere conditions same as the conditions of the case shown in FIG. 19. In this case, the annealing temperature is 400 degrees Celsius.

As shown in FIG. 20, the resistivities increase radically during first 4 minutes 5 since the annealing started regardless of the atmosphere conditions. Then, the resistivities increase gently until 10 minutes. During a period from 10 minutes to 30 minutes, the resistivities are stable.

Accordingly, preferred process time for annealing is 10 to 30 minutes. In other words, the minimum limit should be set to 10 minutes where the radical 10 increase of resistivity stops, and the maximum limit should be set to 30 minutes where the resistivity is stable.

As described above, resistivity of the Ta-Si-O-N heating resistor film is stabilized by annealing. Effects brought by the annealing do not depend on atmosphere differences. Moreover, the effects of the annealing is unchanged 15 even if the heating element is covered. This fact allows the heating element to have a protection layer thereon for producing a highly reliable print head for a thermal ink-jet printer. In this case, the annealing should be done under inert gas or after forming the protection film in order to prevent an adherence layer between the heating element and the protection layer from being oxidized, thus, the 20 protection film is adhered to the heating element firmly.

Various embodiments and changes may be made thereunto without departing from the broad spirit and scope of the invention.

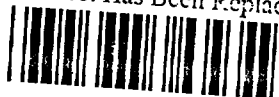
For example, the heating resistor of the present invention may be made of not only Ta, Si, O, and N, but also other elements including, for example, hydrogen or 25 the like.

The purpose of the heating resistor of the present invention is not limited to the thermal ink-jet printer. The heating resistor of the present invention may be used in, for example, a piezoelectric ink-jet printer which utilizes piezoelectric effect, or any products other than the ink-jet printer.

The above-described embodiments are intended to illustrate the present invention, not to limit the scope of the present invention. The scope of the present invention is shown by the attached claims rather than the embodiments.

Various modifications made within the meaning of an equivalent of the claims of 5 the invention and within the claims are to be regarded to be in the scope of the present invention.

This application is based on Japanese Patent Applications Nos. H11-133306 filed on May 13, 1999 and 2000-67612 filed on March 10, 2000 and including specification, claims, drawings and summary. The disclosure of the above 10 Japanese Patent Application is incorporated herein by reference in its entirety.



CLAIMS

1. A heating resistor which emits heat by applying electric current thereto, said heating resistor (12) comprising at least tantalum (Ta), silicon (Si), oxygen (O), and nitrogen (N) as component elements.
- 5 2. The heating resistor according to claim 1, wherein mol% of nitrogen (M2) is $5\text{mol}\% \leq M2 \leq 25\text{mol}\%$.
3. The heating resistor according to claim 2, wherein mole ratio Si/Ta is $0.35 < \text{Si/Ta} < 0.80$.
4. The heating resistor according to claim 3, wherein mol% of oxygen
10 (M1) is $25\text{mol}\% \leq M1 \leq 45\text{mol}\%$.
5. The heating resistor according to claim 1, wherein mole ratio Si/Ta is $0.35 < \text{Si/Ta} < 0.80$.
6. The heating resistor according to claim 1, wherein mol% of oxygen (M1) is $25\text{mol}\% \leq M1 \leq 45\text{mol}\%$.
- 15 7. The heating resistor according to claim 1, said heating resistor comprises amorphous structure, wherein broad peak angle of X-ray diffraction strength appearing in X-ray diffraction is equal to or smaller than 37.5 degrees, and resistivity is equal to or greater than $4\text{m}\Omega\text{cm}$.
8. The heating resistor according to claim 1, said heating resistor
20 comprises amorphous structure, wherein light absorption coefficient at light energy of 0.5 to 1 eV is 70,000/cm or less, and resistivity is equal to or greater than $4\text{m}\Omega\text{cm}$.
9. The heating resistor according to claim 1, wherein said heating resistor (12) is employed in a print head of an ink-jet printer.
- 25 10. The heating resistor according to claim 9, wherein said heating resistor (12) directly contacts ink, and generates a bubble in the ink.
11. A method of manufacturing a heating resistor which emit heat by applying electric current thereto, comprising the steps of:
forming a thin film made of Ta-Si-O-N (12) on a substrate (11); and



forming the heating resistor (12) by annealing said Ta-Si-O-N film (12).

12. The method according to claim 11, wherein the annealing is carried out under the air.

13. The method according to claim 11, wherein the annealing is carried out under inert gas.

14. The method according to claim 11, wherein said heating resistor (12) is employed in a print head of a thermal ink-jet printer, and temperature during the annealing is 350 to 600 degrees Celsius.

15. The method according to claim 14, wherein said print head of the thermal ink-jet printer is a monolithic head in which a head and a drive circuit are mounted on the same silicon substrate, and temperature during the annealing is 350 to 450 degrees Celsius.

16. The method according to claim 11, wherein the annealing is carried out for 10 to 30 minutes.

17. The method according to claim 11, wherein said Ta-Si-O-N film (12) has a protection film (21) thereon, and the Ta-Si-O-N film is annealed.

18. The method according to claim 17, wherein the annealing is carried out under the air.

This Sheet Has Been Replaced



AMENDED CLAIMS

[received by the International Bureau on 22 September 2000 (22.09.00);
original claims 2, 5, 7 and 8 cancelled; original claims 1 and 3 amended;
new claims 19 and 20 added; remaining claims unchanged (2 pages)]

1. (Amended) A heating resistor which emits heat by applying electric current thereto,

said heating resistor (12) comprising at least tantalum (Ta), silicon (Si),
5 oxygen (O), and nitrogen (N) as component elements, and

wherein mol% of nitrogen (M2) is $5\text{mol}\% \leq M2 \leq 25\text{mol}\%$.
2. (Cancelled)
3. (Amended) The heating resistor according to claim 1, wherein mole ratio Si/Ta is $0.35 < \text{Si/Ta} < 0.80$.
- 10 4. The heating resistor according to claim 3, wherein mol% of oxygen (M1) is $25\text{mol}\% \leq M1 \leq 45\text{mol}\%$.
5. (Cancelled)
6. The heating resistor according to claim 1, wherein mol% of oxygen (M1) is $25\text{mol}\% \leq M1 \leq 45\text{mol}\%$.
- 15 7. (Cancelled)
8. (Cancelled)
9. The heating resistor according to claim 1, wherein said heating resistor (12) is employed in a print head of an ink-jet printer.
10. The heating resistor according to claim 9, wherein said heating resistor
20 (12) directly contacts ink, and generates a bubble in the ink.
11. A method of manufacturing a heating resistor which emit heat by applying electric current thereto, comprising the steps of:

forming a thin film made of Ta-Si-O-N (12) on a substrate (11); and

forming the heating resistor (12) by annealing said Ta-Si-O-N film (12).
- 25 12. The method according to claim 11, wherein the annealing is carried out under the air.
13. The method according to claim 11, wherein the annealing is carried out under inert gas.
14. The method according to claim 11, wherein said heating resistor (12) is

AMENDED SHEET (ARTICLE 19)



employed in a print head of a thermal ink-jet printer, and temperature during the annealing is 350 to 600 degrees Celsius.

15. The method according to claim 14, wherein said print head of the thermal ink-jet printer is a monolithic head in which a head and a drive circuit are 5 mounted on the same silicon substrate, and temperature during the annealing is 350 to 450 degrees Celsius.

16. The method according to claim 11, wherein the annealing is carried out for 10 to 30 minutes.

17. The method according to claim 11, wherein said Ta-Si-O-N film (12) 10 has a protection film (21) thereon, and the Ta-Si-O-N film is annealed.

18. The method according to claim 17, wherein the annealing is carried out under the air.

19. (New) A heating resistor which emits heat by applying electric current thereto,

15 said heating resistor (12) comprising at least tantalum (Ta), silicon (Si), oxygen (O), and nitrogen (N) as component elements, and

said heating resistor comprising amorphous structure, wherein broad peak angle of X-ray diffraction strength appearing in X-ray diffraction is equal to or smaller than 37.5 degrees, and resistivity is equal to or greater than $4\text{m}\Omega\text{cm}$.

20 20. (New) A heating resistor which emits heat by applying electric current thereto,

said heating resistor (12) comprising at least tantalum (Ta), silicon (Si), oxygen (O), and nitrogen (N) as component elements, and

said heating resistor comprising amorphous structure, wherein light 25 absorption coefficient at light energy of 0.5 to 1 eV is 70,000/cm or less, and resistivity is equal to or greater than $4\text{m}\Omega\text{cm}$.

