A New Thin Film Heater for Thermal Ink Jet Print Heads

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A new thin film heater for thermal print heads was developed. The thin film heater includes a resistor portion and a conductor portion that supplies voltage to the resistor. The resistor portion has a thin insulating self-oxidizing coat, which prevents oxidation and electrolytic corrosion by ink, so the thin film heater does not require a thick overcoat. The anode side of the conductor is covered with an ink barrier layer, so electrolytic corrosion is prevented. Furthermore, a print head structure that does not generate cavitation was developed, and it was shown that the thin film heater could be used in this print head. The heater requires remarkably little energy to eject ink droplets. Also, the heater rapidly heats up the ink, which translates into more uniform velocity of ejected ink droplets.

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Introduction

The thermal ink jet printer was developed commercially through energetic research and development by Canon Inc. and Hewlett Packard Co. Today this technology dominates most low-speed printer applications. Furthermore, Micro Fine Droplet Technology[1] introduced in 1999 suggested the possibility that the thermal ink jet printer could evolve even further.

We developed similar technology, and predicted that in the near future the thermal ink jet printer would probably replace laser beam printers in the high-speed category.[2,3] The technologies that we developed are as follows.

(1) a thin film heater that does not need thick protection layers,[3-5]
(2) a head structure that ejects ink droplets of substantially uniform volume[5,6] and wherein cavitation is not generated,[5,7]
(3) a production method for print heads that have large scale integrated (LSI) nozzles,[2,8] and
(4) a rapid dry printing system that also achieves bleedless printing.[9]

This article focuses on the new thin film heater.

Outline of New Thin Film Heater

A thin film heater consists of a thin film resistor and a thin film conductor. When used in a thermal ink jet print head, thin film heaters must withstand oxidation, electrolytic corrosion, and cavitation in ink. Conventional thin film heaters are covered with a thick passivation layer and a tantalum metal layer for protection against these problems. However, this multilayer overcoat greatly reduces the thermal efficiency of the heater, so a great deal of energy is required to eject ink droplets. As a result, the driver LSI used for the heater substrate must use expensive Bi-CMOS technology. Furthermore, this multilayer overcoat reduces the speed at which ink is heated, so the velocity of ejected ink droplets[10] can fluctuate.

In order to improve these conventional drawbacks, we developed a thin film resistor with a thin insulating self-oxidizing coat that can prevent oxidation and electrolytic corrosion. Next, we developed a thin film conductor that is not corroded by ink and a method for covering the anode side of the conductor with an ink barrier layer to prevent electrolytic corrosion. With these developments, the new thin film heater does not need a thick multilayer overcoat. Furthermore, a head structure that does not generate cavitation was developed and we showed that the thin film heater could be used as part of the head structure. The thin film heater requires a remarkably small amount of energy to eject ink droplets, so inexpensive CMOS technology can be used for the driver LSI. This enables a reduction in production costs of print heads to almost half that of conventional print heads. Moreover, ink can be heated much more rapidly, so ink droplets can be ejected at more uniform speeds. Details are reported below.

Ta-Si-O Ternary-Alloy Thin Film Resistor

Through previous research, we developed a Cr-Si-O ternary-alloy thin film resistor for thermal print heads.[11] This resistor maintains a stable resistance value even when heated in air by application of voltage pulses. We heated this thin film resistor to a high temperature to form a self-oxidizing insulating coat on its surface. However, we found that the self-oxidizing coat was unsatisfactory because it was semiconductive and subject to the electrolytic corrosion in ink. We replaced the chromium

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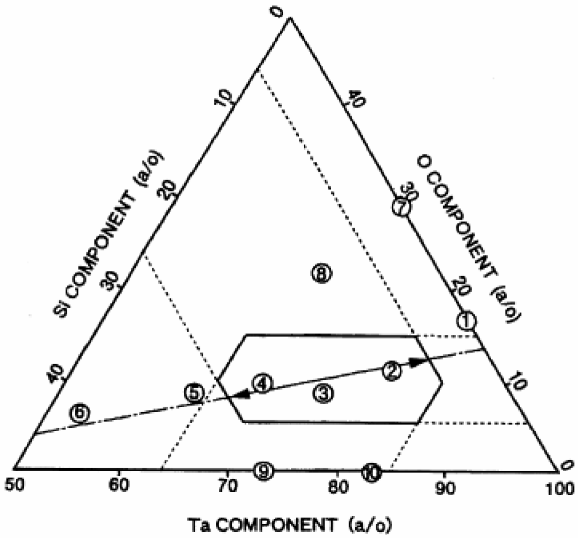

Figure 1. Ta-Si-O ternary-alloy composition diagram and evaluated samples.

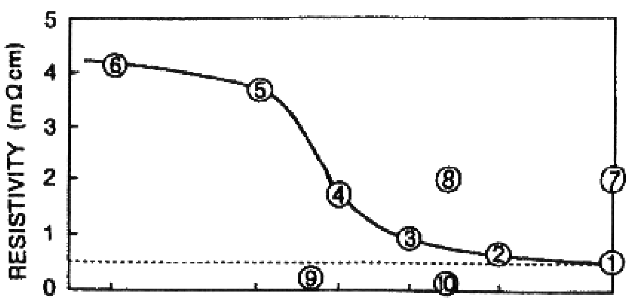

Figure 2. Specific resistivity of as sputtered films.

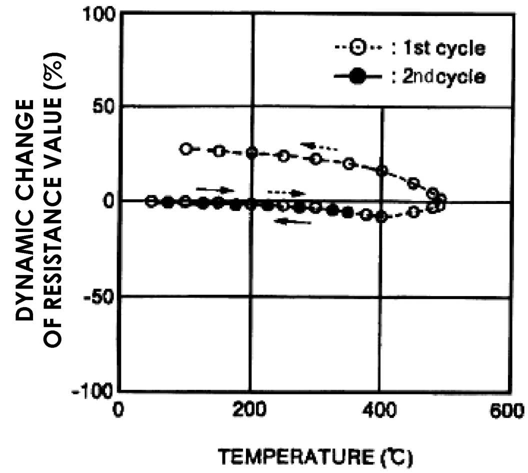

Figure 3. The change rate of resistance value of sample **3** by heating and cooling in the air.

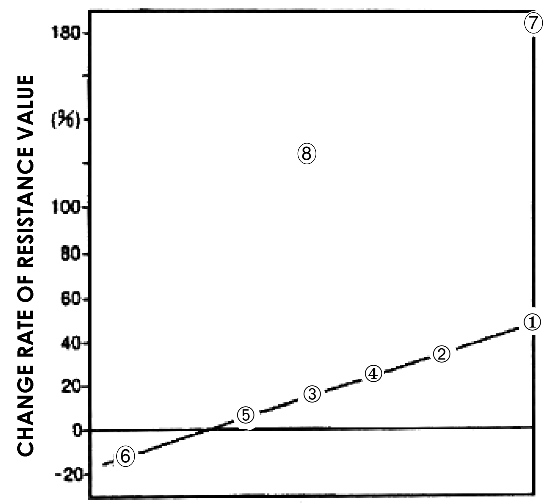

Figure 4. Change rate of resistance value resulting from the thermal oxidation at 500°C for 10 minutes.

component of the ternary-alloy with tantalum, and heated it in the manner described above. In this case, an insulating coat with thickness of about 10 nm was formed on the surface by the thermal oxidation process.

Production Method

The Ta-Si-O ternary-alloy thin film was deposited on a thermally oxidized silicon wafer by reactive sputtering in a partial pressure oxygen gas environment. The sputter target was prepared by carving trenches in a tantalum target and filling the trenches with silicon slips. The composition ratio of the ternary-alloy thin film was controlled by changing the width of the silicon slips and the partial pressure of the oxygen gas. The composition ratio of the deposited thin film was identified by chemical analysis and Auger electron spectroscopy.

Although we evaluated different compositions over a wide range, this report focuses on the ten samples represented in the chart of Fig. 1. The compositional rates of samples **1** ~ **6** are plotted along a straight line in Fig. 1. We evaluated various characteristics as tendencies resulting from alignment with the line. Tendencies resulting from compositional rates above and below the line were deduced from the characteristics of **7**, **8** and **9**, **10**.

Basic Characteristics

Figure 2 shows the specific resistivity of sputtered thin films with thickness of about 100 nm. Usually, heaters used for top shooter type print heads have a square shape. The thin film resistors must be more than 50 nm thick to be of practical use. Furthermore, the resistance value of a thin film heater needs to be about 100 Ω or more considering the electric current capacity of the LSI driver used for the heater substrate. Considering those requirements, the thin film resistor needs to have a specific resistivity of more than 0.5 m Ω-cm. Samples **9** and **10** do not meet this requirement.

Figure 3 shows the resistance change of the sample **3** through a heating cycle wherein the sample was maintained at 500°C for 10 minutes and then cooled down in air. The solid line shows the change for a second heating cycle with high temperature of 350°C. We found that the resistance value was very stable, so that no change was observed, as long as the re-heating temperature was below the highest thermal oxidation temperature. We believe that this thermal oxidation is limited only within the surface layer of the thin film resistor.

Figure 4 shows the rate of resistance change after thermal oxidation. A large rate means that thermal pro-

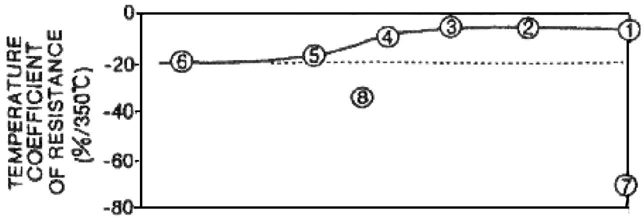

Figure 5. Average temperature coefficient of resistance between 20°C and 350°C after oxidation at 500°C.

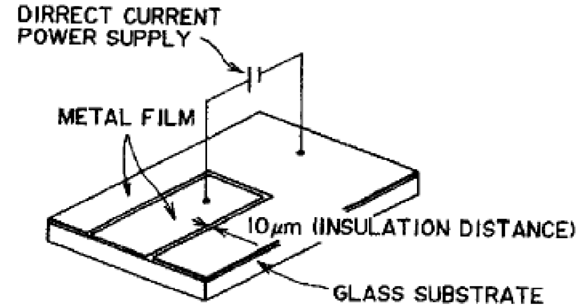

Figure 7. Electrolytic corrosion test configuration.

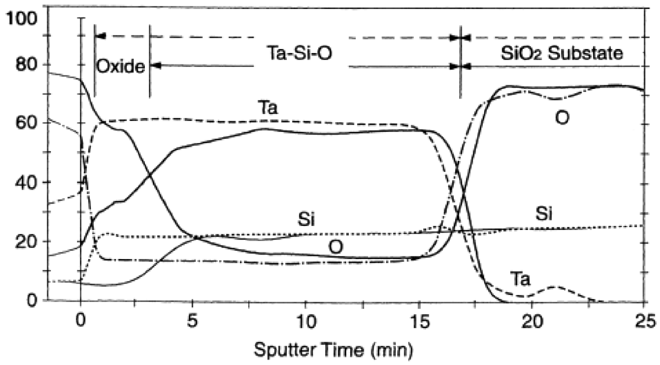

Figure 6. AES depth profile of Ta-Si-O resistor **3** (solid: after oxidation, dotted: as deposition).

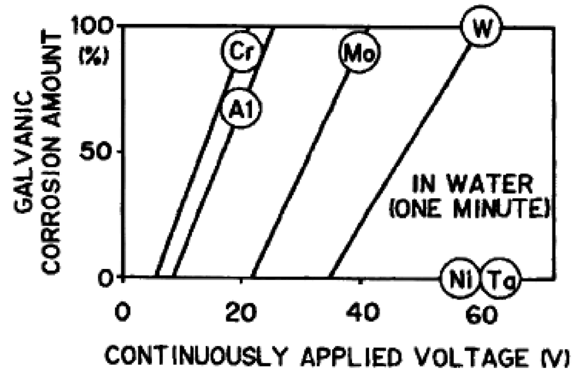

Figure 8. Corrosion amount against applied voltage.

cessing will change the resistance values of heater arrays with great variation between different heaters. For this reason, a large rate is not desirable, and the samples **1**, **7**, and **8** will be excluded from further discussion.

As shown in Fig. 3, this thin film resistor has a negative temperature coefficient. Figure 5 shows the average temperature coefficient of these samples between 20°C and 350°C, after thermal oxidation at 500°C. When used in a print head, the resistor array is driven at a controlled voltage by an LSI driver circuit. Therefore, a large negative temperature coefficient of the resistor results in the resistor temperature rapidly increasing and will result in thermal runaway. From this viewpoint, samples **5** and **6** are undesirable and will be omitted from further discussion.

Figure 6 shows the depth profiles of the thin film composition of the sample **3** before and after thermal oxidation at 500°C for 10 minutes, as measured by Auger Electron Spectroscopy (AES). As can be determined from Fig. 6, the depth of the self-oxidizing layer on the film surface is almost limited to within about 15 nm. This is consistent with the results shown in Fig. 3.

In conclusion, the usable composition range of the ternary alloy thin film is within the area enclosed by the solid line shown in Fig. 1.

The thin film heaters are formed on a LSI chip when used in a print head. Therefore, it is necessary to perform the thermal oxidation processing of the heater array at a temperature that does not affect the LSI circuit. On the other hand, this temperature must be higher than the nucleate boiling temperature of ink. The various characteristics mentioned above were confirmed not to change, even when the thermal oxidation temperature is set as low as 400°C. From the above consideration, the thermal oxidation temperature was set to 400°C.

Nickel Thin Film Conductor

In order to produce a thin film heater that does not need any overcoats, a thin film conductor material is required that is not corroded in ink. Since metal is generally corroded by the micro battery effect, we performed electrolytic corrosion tests to evaluate the suitability of different conductor materials. Each metal thin film sample was formed to a thickness of 100 nm on a glass substrate using the sputtering method. Each sample was photoetched to form a 10 μm groove, in order to divide the sample into two portions as shown in Fig. 7.

As shown in Fig. 7, we applied a constant voltage for 1 minute to each sample underwater and then measured the area of the electrolytically corroded portion of the metal thin film. Fig. 8 shows the area that was electrolytically corroded by different voltages for six kinds of metals. We found that nickel and tantalum had outstanding anti-corrosion characteristics. Of those, nickel was selected, because nickel enables selective etching of a Ta-Si-O ternary-alloy thin film.

Although details are omitted, this nickel thin film is the optimal material also for attaining a secure connection and high reliability of bonding pads of the driver LSI at low cost.[12]

Nucleate Boiling by Ta-Si-O/Ni Thin Film Heater

We deposited a Ta-Si-O ternary-alloy thin film, which had almost the same composition as the sample **3**, on the thermally oxidized Si substrate to the thickness of about 100 nm and, within the same sputter equipment, further deposited a nickel thin film to the thickness of

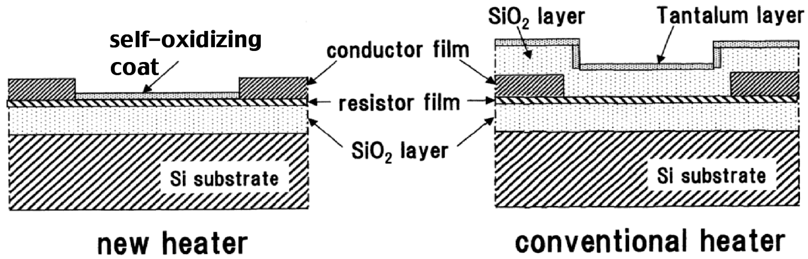

Figure 9. Sectional drawings of the new heater and conventional heater.

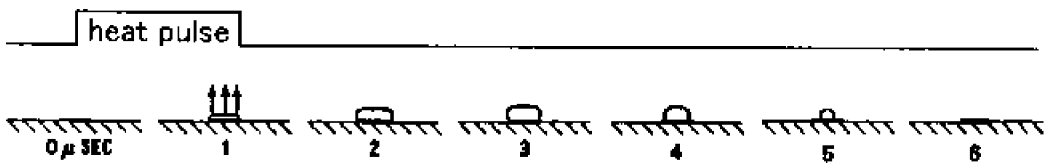

Figure 10. Sketch chart of stroboscopic observation of open pool boiling.

500 nm. We photoetched the thin film into square-shaped heaters with sides 35 μm long and heated the heaters at 400°C for 20 minutes in oxygen gas. The resistance values of these heaters were about 100 Ω. Figure 9 compares the cross section of the new heater with a conventional heater. The following experiments were conducted in the pure water, so that nucleate boiling could be more easily observed.

Open pool Boiling

The new heater was pulse heated in pure water to generate nucleate boiling. This is referred to as open pool boiling. The minimum electric power required for boiling was about 1.3 W at a pulse width of 1 μsec. This threshold energy is about one-tenth the power required for a conventional heater. This threshold energy is even smaller for heaters made on a LSI substrate. Because the thickness of the SiO_2 layer under the heater can be thickened to about 2 μm, which is about twice compared with the case of a thermally oxidized silicon substrate.

Here, some facts known about nucleate boiling will be briefly explained. First, when pure water is heated using a defect-less heater such as a thin film heater, nucleate boiling starts only after the temperature reaches 260°C or more. This is called "spontaneous nucleate boiling". When the heating rate is under 70 million °C/sec, boiling nucleus density is comparatively low and the position of the nucleus on the heater also fluctuates. As a result of this fluctuation, the vapor bubble tends to grow in an anisotropic manner with each pulse of the heater. This results in poor consistency in ejecting velocity of ink droplets, so that printing quality is poor.[10] On the other hand, if the heating rate exceeds this critical point, the boiling nucleus density becomes very high and the boiling nuclei are uniformly generated across the entire heater surface. We will refer to this boiling phenomenon as caviar-like nucleate boiling,[13] because the numerous boiling nuclei appear like caviar (small spheres) spread across on the heater surface. Caviar-like nucleate boiling is an important condition for stabilizing the ejecting velocity of ink droplets.[14] The thick overcoats of a conventional heater make it impossible to attain this critical point, even if a short drive pulse of sub-μsec is applied.

Figure 10 shows caviar-like nucleate boiling that occurs at a heating rate of about 300 million °C/sec. Although details are omitted, the temperature when caviar-like nucleate boiling occurs is about 300°C. Also, only water that is within about 10 nm from the heater surface boils. The saturated vapor pressure is initially about 8 MPa (80 atm) and this pressure pushes up the water on the heater to the height of about 25 μm at the initial velocity of 20-25 m/sec. However, the bubble vapor rapidly cools and condenses to a vacuum state in 1-2 μsec by adiabatic expansion, and the bubble starts to shrink. The bubble continues to shrink without changing its height. Cavitation occurs when the bubble collapses, and leaves destructive marks of sub-μm size on the heater surface.[15] A bubble takes the same amount of time to reach its maximum size regardless of the heater size, but collapses more rapidly with smaller heater size.

Mechanical Stress That Accompanies Nucleate Boiling

We attached a small acoustic emission sensor to the back of a heater substrate, and measured the mechanical stress that occurs during open pool boiling.[7]

Figure 11 shows the acoustic emission signal when the water depth on the heater is 1 mm. The first peak represents the initial pressure of about 8 MPa exerted across the entire heater when a bubble generates. The following larger peak represents mechanical stress that occurs when the bubble collapses. This mechanical stress is concentrated and exerted on a sub-μm area around the center of the heater. Therefore, the mechanical stress from cavitation is sufficiently large to fracture a hard oxide.

Next, we show that this mechanical stress changes greatly depending on the depth of water on the heater. We measured mechanical stress that resulted from bubble generation, while gradually decreasing the depth of water on the heater by air drying. The result is shown in Fig. 12. The mechanical stress from bubble generation decreases as the depth of water becomes shallower, but the mechanical stress from cavitation rapidly decreases when the water depth is about 40 μm, and becomes zero when the water depth is about 25 μm. From this result, we believe that when the water depth on

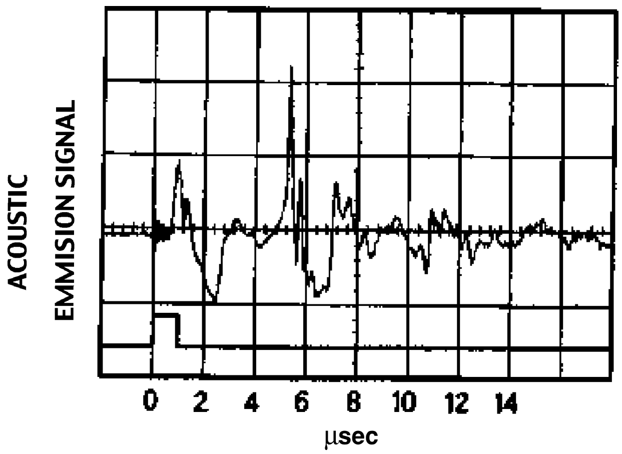

Figure 11. Acoustic emission signal obtained at open pool boiling when the water depth is 1 mm.

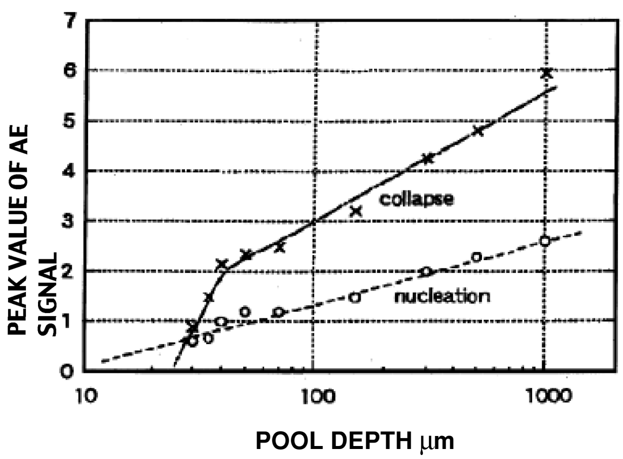

Figure 12. Peak values of AE signals versus open pool depth.

the heater is around 25 µm or less, the bubble merges with the open air before it reaches the maximum size, thus preventing cavitation.

We also performed experiments with the heaters surrounded by an ink barrier or orifice plate to generate so-called closed pool boiling. It is known that the pulse lifetime is extended greatly in closed pool boiling conditions.[15] We confirmed this from another viewpoint by the following experiments.[7]

As shown in Fig. 13, we formed a top shooter type device on a Si substrate. The device includes a heater and a cylindrical nozzle. We then formed the same kind of heater, separately on the same Si substrate in an open boiled situation. We attached an acoustic emission sensor at the middle point on the back of the substrate. We covered the open pool heater with water to the same depth as in the ink jet device, and applied voltage pulses under the same conditions for both the open pool heater and the top shooter type device. Thus, we were able to measure mechanical stresses generated by both open pool boiling and closed pool boiling under the same conditions for water depth and for the heater.

The experimental results are shown in Fig. 14. The device showed little mechanical stress, so Fig. 14 shows

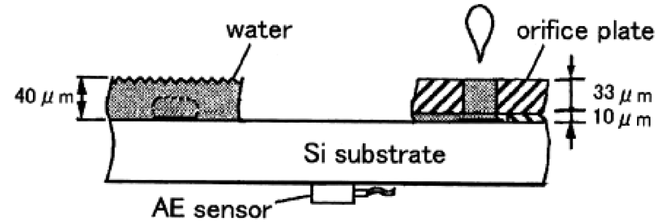

Figure 13. Sample configuration for measuring mechanical stresses of open pool boiling and closed pool boiling.

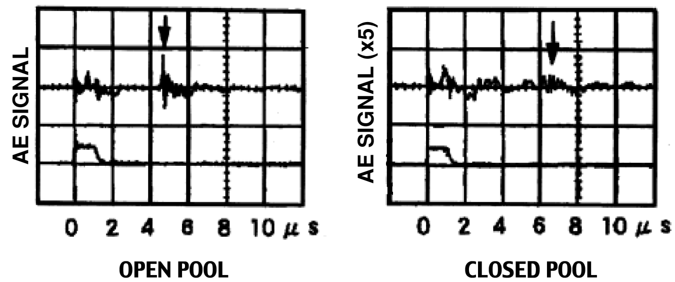

Figure 14. Mechanical stresses for open pool boiling and closed pool boiling with the same water depth.

the acoustic emission signal magnified five times. Although the water depth was the same, the device generated much less mechanical stress, that is, one quarter during bubble generation and one-fifteenth during bubble collapse. Bubble generation generated little stress because the water pressure on the heater was reduced by the capillarity of the nozzle. Bubble collapse generated even less stress because the bubble merged with the open air after the ink droplet is ejected. We performed experiments to confirm these points. We filled the orifice plate surface of the above device to about 20 µm deep and repeated the same experiment. As a result, the observed mechanical stress was the same level as in open pool boiling with a water depth of about 60 µm. These results show the possibility of a device structure that can prevent cavitation. The production method of the device shown in Fig. 13 is described briefly below.

Application of Ta-Si-O/Ni Thin Film Heater to Print Heads

Life Test in Open Pool

First, we evaluated the life of the new heater in open pool boiling. The water depth on the heater was made comparatively deep to 1 mm to 2 mm so that it would not change during the experiments. We set the width of the driving pulse to 1 µsec and the repetition frequency to 1 kHz. As a result, defects were observed at the central part of the heater after 1 ~ 2 million pulses and damage prevailed over the entire heater. This contrasts with the heater of the commercially available head, which can be driven by 10 to 20 million pulses before showing similar damage. The longer life of the conventional heater comes from the thick overcoats. The life of the new heater can be extended much further by lowering the water depth, but with greater variation between different heaters. We will describe the life characteristics of the new heater when used in print heads later. Little difference in life was observed when commercial

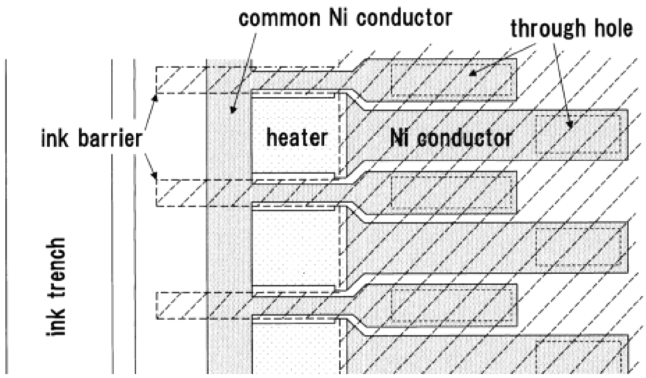

Figure 15. Protection method for anode side thin film conductors.

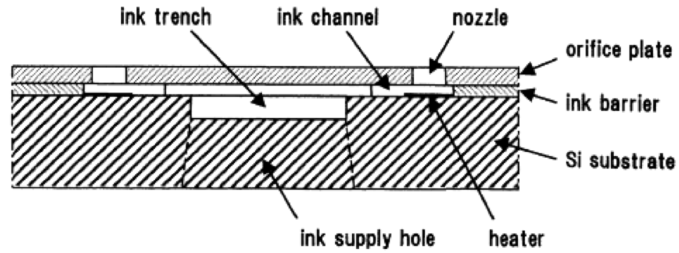

Figure 16. Sectional diagrams of the trial head.

ink was used instead of pure water in open pool tests. However, electrolytic corrosion appeared, although only on the anode side of the thin film conductor. Therefore, preventing this electrolytic corrosion became the first requirement for practical use of the new heater.

Protection Method of Anode Side of Conductor

The most effective method[5,16] to protect the anode side of the conductor from electrolytic corrosion is to cover it with an ink barrier layer including a part of the thin film resistor. This configuration is shown in Fig. 15. In this case, an ink barrier layer made from a heat-resistant organic material has a smaller heat transfer rate than that of ink. The thin film resistor heats up about 15% hotter where covered with this barrier layer than the uncovered heater portion. Taking the variation seen in resistance values of heater arrays into consideration, we believe that the highest temperature of the covered portion reaches about 400°C. Therefore, it is necessary to lower this temperature by about 15% even when polyimide is used as the ink barrier material, despite its excellent heat-resisting properties.

Thus, as shown in Fig. 15, we extended the width of the resistor portion covered with the barrier layer and its nearby area by about 10%, thereby decreasing the exothermic density of this portion by about 20%. Fig. 15 shows that an ink trench is formed in the Si substrate for ink supply. Also, through-holes are provided for connecting the heaters to the LSI circuits which selectively drive the heater array.

Design Philosophy for Print Head

Here the design philosophy and the method of producing the print head will be discussed briefly with reference to Fig. 16.

(1) A top shooter type print head was selected because many nozzle arrays can be formed on a single chip LSI.

(2) The head nozzle should be designed with a structure capable of separating the ejected ink from the ink supply channel and capable of ejecting ink directly. This structure prevents cavitation because a bubble merges with the open air. Ink droplets are ejected at a consistent volume that is proportional to the volume of the ink on a heater and that is independent from the ink temperature.

(3) To achieve this, the nozzle should be located directly above the heater. Additionally, the bottom edge of the nozzle should have an aperture that is smaller than the size of generated bubbles. That is, the diameter of the nozzle should be the same or smaller than the heater size. The nozzle top should be separated from the heater surface by a distance equal to or less than the maximum growing height of the bubble in open pool boiling.

(4) The nozzle should have a linear shape, such as a cylindrical barrel in order to stabilize the ejecting direction of ink droplets. Nozzles can be linearly formed by photo dry etching an orifice plate that is laminated on an ink barrier layer.

Although details[8,12] of the production method are beyond the scope of this paper, we would like to mention that only photo etching process[17,18] is used to form the print heads. This enables the large scale integration of minute nozzles in a high density on a CMOS LSI wafer. However, we used a thermally oxidized Si wafer for the heater substrate in our experiments. At the time we performed the print head experiments described above, only polyimide film of thickness 33 µm (including the adhesion layer) was available as an orifice plate film. When a film of thickness 20 µm became available we made print heads using the thinner film and again tested the life of the heater.

Lifetime of the Heater on Trial Head

We tested the above head filled with an ink currently sold for ink jet printers. However, when the heater was used to eject ink, it broke down after about 100 million pulses. Furthermore, there was great variation in the life of different heads. We believe that the bubble imperfectly merged with atmosphere because the nozzle top was separated from the heater by as much as 43 µm. This consideration was also supported by the fact that mechanical stress, though small, was observed at bubble collapse as described in the previous section. As an additional experiment, we evaluated a print head with a thinner orifice plate of 20 µm. No abnormalities on the heater were observed even after 200 million ink ejections. Moreover, we raised the head temperature, but no influence on the printing density was observed. This shows that the volume of ejected ink droplets is very stable, as we expected.

Optimization of Driving Pulse Width

We varied driving pulse width of the heater and measured the ejecting velocity of ink droplets. The result is shown in Fig. 17.

The ejecting velocity was inconsistent when the heating rate was lower than 100×10^6 °C/sec, but stabilized at higher heating rates. This shows that caviar-like nucleate boiling is an important condition for stable ejection of ink droplets as mentioned before. However, ejecting velocity began to fall when the heating rate exceeded

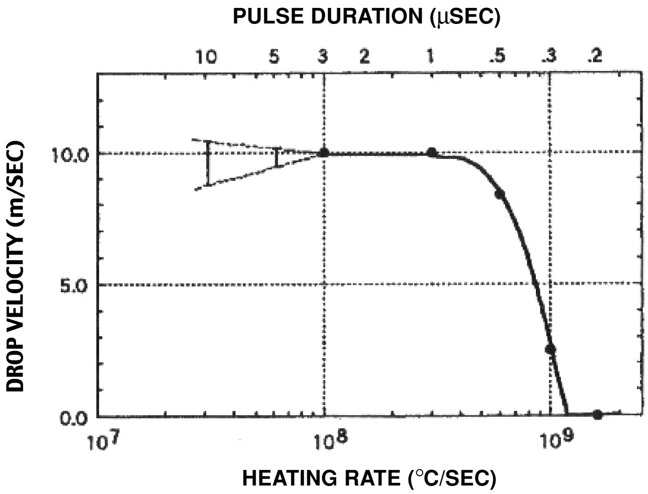

Figure 17. Drop velocity versus heating rate.

300×10^6 °C/sec. Ejection itself was impossible at a heating rate above 1×10^9 °C/sec.

We suggest the following reasons. Only ink that is close to the heater surface boils at high heating rates. In other words, less ink participants in nucleate boiling at high heating rates so that less ejection energy is generated. This idea is supported by stroboscope observations showing that smaller bubbles are generated at high heating rates in open pool boiling.[14] Fast and stable ejecting velocity of ink droplets is desirable for ink jet printers. That is, the heating rate of the heater optimally 100×10^6 °C/sec. This translates into a pulse width of about 3 µsec for the driving pulse of the new heater. In this case, the driving power and the driving current are much lower than for a shorter pulse width, so that a CMOS LSI can easily be adopted as a driver circuit.

Conclusions

A thin film resistor that can form an insulating self-oxidizing coat on its surface was developed. A corrosion-resistant thin film conductor was explored, and a method was developed for protecting against electrolytic-corrosion in ink by covering the anode side of the conductor with an ink barrier layer. The thin film heater made of such materials did not need any additional protection layers, and it turned out that the driving power required for the ejection of an ink droplet could be reduced to one-tenth or less that of the conventional heaters. The mechanical stress developed in the heater from nucleate boiling was evaluated quantitatively. A practical device structure was developed and shown to be capable of ejecting ink droplets with consistent volume and to be free from generation of cavitation. The new heater used in this device was tested to up to 200 million pulses without problem. Finally, it was shown that the optimal driving pulse width of 3 µsec requires the minimum driving power while maintaining high speed and stable ejection of ink droplets.

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