Hybrid functional IrO$_2$-TiO$_2$ thin film resistor prepared by atomic layer deposition for thermal inkjet printheads

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Received 21 April 2010; accepted 10 September 2010

Abstract: IrO$_2$-TiO$_2$ thin films were prepared by atomic layer deposition using Ir(EtCp)(COD) and titanium isopropoxide (TTIP). The resistivity of IrO$_2$-TiO$_2$ thin films can be easily controlled from 1500 to 356.7 $\mu$Ω·cm by the IrO$_2$ intermixing ratio from 0.55 to 0.78 in the IrO$_2$-TiO$_2$ thin films. The low temperature coefficient of resistance (TCR) values can be obtained by adopting IrO$_2$-TiO$_2$ composite thin films. Moreover, the change in the resistivity of IrO$_2$-TiO$_2$ thin films was below 10% even after O$_2$ annealing process at 600 °C. The step stress test results show that IrO$_2$-TiO$_2$ films have better characteristics than conventional TaN$_{0.8}$ heater resistor. Therefore, IrO$_2$-TiO$_2$ composite thin films can be used as a heater resistor material in thermal inkjet printhead.

Key words: IrO$_2$-TiO$_2$ film; heating resistor; inkjet

1 Introduction

In recent years, the inkjet printer has emerged as one of the main-stream digital printing techniques. Inkjet technologies are usually divided into continuous and drop-on-demand (DOD) printing methods[1]. Among them, the majority of activity in inkjet printing today is in the DOD methods because of their low cost and high printing quality, and color capability[2]. In the thermal inkjet printer, a thin film resistor heater which converts an electrical energy into a thermal energy is generally used to eject the ink. However, because it is subjected to severe environments such as high operation temperature, chemical attack by the ink, and mechanical stresses arisen from cavitation forces during the operation[3], the choice of adequate heater materials is very important for the application of inkjet printhead.

Therefore, the heater resistor material should have a sufficient resistivity range (>150 $\mu$Ω·cm) for making heater layers of controllable thicknesses[3], and a near-zero temperature coefficient of resistance (TCR) for the stable ejection of the ink. In addition, it should have a strong resistance against both corrosion and oxidation to prevent the degradation of the inkjet printhead and a good adhesion property to the underlying SiO$_2$ thermal insulation layer.

Up to now, several materials have been considered in the printhead, such as polysilicon, HfB$_2$, Ta-Al and TaN[3−10]. To protect these heater resistor films against physical or chemical attacks, the passivation layers such as SiN, SiC and Ta are generally used. However, the required onset power for bubbling with these passivation layers is higher than that without passivation layers[11]. Therefore, in order to increase the heat efficiency, the passivation layers should be thinned as possible or removed. However, it should be noted that the above-mentioned heater materials such as polysilicon, HfB$_2$, Ta-Al and TaN can not be used without the passivation-layers because they are easily oxidized and corroded at the operation environmental conditions without passivation layers. Recently, it was reported that atomic layer deposited RuO$_2$-TiO$_2$ has many attractive properties for using it as a heating resistor such as appropriate resistivity range with a sufficiently low temperature coefficient of resistance (TCR) values and high oxidation resistance even at high temperatures[12]. However, RuO$_2$-based heating resistor films have a potential problem for a heating resistor application because RuO$_2$ phases are easily decomposed to volatile...
RuO₄ phases above 800 °C[13].

In this study, we investigated IrO₂-TiO₂ thin film resistor prepared by atomic layer deposition method as an alternative of RuO₂-TiO₂ thin films. Similar to RuO₂, IrO₂ also has low resistivity and good oxygen diffusion barrier properties[14]. Compared with Ru, the volatile phases of Ir form at above 1 000 °C, and no phase transformations are known in the temperature range from 4.2 to 1 000 K[14−15], which means that IrO₂ remains more stable than RuO₂ at higher annealing temperatures.

2 Experimental

IrO₂-TiO₂ films were grown on 1 300 nm-thick SiO₂ film formed on Si substrates with ALD at a temperature of 230 °C and a pressure of 400 Pa. Titanium isopropoxide (TTIP) and (Ethylcyclopentadienyl) (1, 5-cyclooctadien) iridium (Ir(EtCp)(COD)) were used as Ti and Ir precursors, respectively. TTIP and Ir(EtCp)(COD) were heated at 50 °C and 85 °C, respectively. During the deposition, 100 cm³/min Ar gas was continuously supplied into the reactor. IrO₂-TiO₂ films were deposited by repeating a super-cycle, which consisted of two groups of sub-cycle dedicated for IrO₂ and TiO₂, respectively. Also, a sub-cycle consisted of several unit cycles, and in a unit cycle, four consecutive pulses were supplied. A unit-cycle for TiO₂ was composed of TTIP vapor pulse with 50 cm³/min Ar carrier gas, a purge pulse with 50 cm³/min Ar, NH₃ pulse with 25 cm³/min, and another 50 cm³/min Ar purge pulse, and a unit-cycle for IrO₂ was composed of a Ir(EtCp)(COD) vapor pulse with 50 cm³/min Ar carrier gas, a purge pulse with 50 cm³/min Ar, a O₂ pulse with 200 cm³/min, and another 50 cm³/min Ar purge pulse. Table 1 summarizes the supercycle design for ALD IrO₂-TiO₂ thin films. The six samples of IrO₂-TiO₂ thin films were prepared and labeled as A: (IrO₂)₀.₃₃-(TiO₂)₀.₆₇, B: (IrO₂)₀.₅₆-(TiO₂)₀.₄₄, C: (IrO₂)₀.₆₄-(TiO₂)₀.₃₆, D: (IrO₂)₀.₇₂-(TiO₂)₀.₂₈, and E: (IrO₂)₀.₇₈-(TiO₂)₀.₂₂, respectively. These samples were prepared by adopting an adequate super-cycle for IrO₂-TiO₂ ALD, which is composed of IrO₂ and TiO₂ subcycle.

The film thickness was measured with field emission scanning electron microscopy (FESEM), and the film composition was analyzed using 9.0 MeV He²⁺ Rutherford backscattering spectroscopy (RBS) and Auger electron spectroscopy (AES). The microstructures of the films were determined by X-ray diffraction (XRD). For evaluating the electrical characteristics, the sheet resistance of the films was measured through a four-point probe test. The rapid thermal annealing (RTA) was also performed on the as-deposited films in the O₂ ambient for 30 min to investigate the thermal stability and oxidation resistance properties of IrO₂-TiO₂ thin films. After RTA process, the changes in the sheet resistance were measured by four-point probe test. In order to evaluate the TCR properties of the films, sputtered aluminum electrode (100 nm) was patterned on the IrO₂-TiO₂ (100 nm)/SiO₂ (1 300 nm)//Si (100) substrate using a shadow mask with the interval of about 100 μm between Al dots, and the TCR values were measured through heating procedure from 25 to 170 °C in a thermostatically controlled oven using a digital multimeter (HP3457A).

3 Results and discussion

Figure 1 shows the electrical resistivities of the IrO₂-TiO₂ thin films depending on the IrO₂ intermixing ratio. When the IrO₂ intermixing ratios of the film were lower than 0.56, the film resistivity was increased drastically with decrease in the IrO₂ intermixing ratio. When the IrO₂ intermixing ratios in IrO₂-TiO₂ thin films are over 0.56, the film resistivity did not undergo a steep rate of change with increasing the IrO₂ intermixing ratio. For the IrO₂ intermixing ratios in the range of 0.56−0.78, the resistivity of the films can be controlled from 1500 to
356.7 μΩ·cm. Initially, the film resistivities were observed to be very high due to the high contents of the highly resistive TiO₂. However, the film resistivities decreased gradually as the intermixing ratio of IrO₂ increased, because IrO₂ is a conductive oxide with a lower electrical resistivity of 40 μΩ·cm.

Figure 2 shows the TCR characteristics of as-deposited IrO₂-TiO₂ thin films. At IrO₂ intermixing ratios of less than 0.56, the TCR values of the films decreased drastically up to −1.500×10⁻⁶/K (sample A). These TCR values are far too low to allow the use of these films in heating resistors. With a thin film resistor having a high TCR, uniform heating rate is hard to be obtained. When the IrO₂ intermixing ratios were higher than 0.56, the TCR values slowly varied from −420×10⁻⁶/K (sample B) to −75.35×10⁻⁶/K (sample E). With appropriate intermixing ratios (Samples C, D and E), the IrO₂-TiO₂ thin films showed lower absolute values of TCR values than TaN₀.₈ (336.1×10⁻⁶/K)[12]. From the results of resistivity and TCR values, samples C, D, and E can be utilized as alternative heating resistor films.

![Figure 2](image2.png)

**Fig.2** Variation of TCR values of IrO₂-TiO₂ thin films depending on IrO₂ intermixing ratios (Temperatures were varied from 25 to 175 °C)

Figure 3 shows the XRD patterns of the as-deposited 50 nm-thick IrO₂-TiO₂ thin films depending on the IrO₂ intermixing ratios. In order to compare the differences in phase, the XRD patterns of a pure TiO₂ and RuO₂ films were included. The as-deposited IrO₂ and TiO₂ films showed clear diffraction peaks, indicating that both films had a poly-crystalline structure. However, none of the IrO₂-TiO₂ thin films (samples A, B, C, D, E, and F) exhibited distinct diffraction peaks, indicating that the films are nanocrystalline amorphous.

Since there is small solubility between IrO₂ and TiO₂[16], the resistivity of the films can be changed because heating resistors are utilized at higher temperatures. Therefore, we investigated the effect of O₂ annealing on the resistivities of IrO₂-TiO₂ films, as shown in Fig.4. The O₂ annealing was performed on the samples at various temperatures for 30 min. Although some solubility of TiO₂ in IrO₂ exists, the change in resistivities of IrO₂-TiO₂ films was below 10%, which means that IrO₂-TiO₂ thin films can be utilized as a stable heating resistor at a high temperature operation without an additional passivation layers.

![Figure 3](image3.png)

**Fig.3** XRD patterns of as-deposited IrO₂-TiO₂ thin films prepared by atomic layer deposition

![Figure 4](image4.png)

**Fig. 4** Variation of sheet resistance of IrO₂-TiO₂ thin films depending on O₂ annealing temperatures

### 4 Conclusions

The IrO₂-TiO₂ thin films with low TCR values and appropriate resistivities for heating resistor applications were prepared by controlling the intermixing ratios. The TCR values of the IrO₂-TiO₂ thin films were maintained at (−420 −75.35)×10⁻⁶/K by varying the IrO₂ intermixing ratios from 0.56 to 0.78, with resistivities remaining in the range of 1 500 − 356.7 μΩ·cm. Also, the IrO₂-TiO₂ thin films showed minimal resistivity change even after O₂ annealing process at 600 °C. Therefore, IrO₂-TiO₂ thin films can serve as a suitable heating resistor material for non-passivated
thermal inkjet printhead applications.

Acknowledgements

This work was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea. This work was also supported by Basic Science Research program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0001-226).

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(Edited by YUAN Sai-qian)