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ORIGINAL PAPER

Hybrid functional RuO_2–Al_2O_3 thin films prepared by atomic layer deposition for inkjet printhead

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Abstract Hybrid functional RuO_2–Al_2O_3 thin films were prepared by atomic layer deposition using bis(ethylcyclopentadienyl)ruthenium ($Ru(EtCp)_2$) and trimethyl aluminum (TMA). The intermixing ratios between RuO_2 and Al_2O_3 in the RuO_2–Al_2O_3 thin films were controlled from $(RuO_2)_{0.16}$–$(Al_2O_3)_{0.84}$ to $(RuO_2)_{0.72}$–$(Al_2O_3)_{0.28}$. With the RuO_2 intermixing ratio less than 0.43, both temperature coefficient of resistance (TCR) values and resistivities were abruptly changed. The TCR values for RuO_2–Al_2O_3 thin films were changed from −381 to −62.3 ppm/K by changing the RuO_2 intermixing ratios from 0.43 to 0.83, while the resistivities were also changed from 1,200 to 243 μΩ·cm. Moreover, the change in the TCR of RuO_2–Al_2O_3 thin films was below 127 ppm/K even after O_2 annealing process at 700 °C. Moreover, it showed that RuO_2–Al_2O_3 thin films had a high corrosion resistance due to the highly corrosion-resistive RuO_2 and Al_2O_3.

Keywords Atomic layer deposition · RuO_2–Al_2O_3 · Corrosion · Inkjet printhead

Introduction

In recent years, the thermal inkjet (TIJ) printer has emerged as one of the mainstream digital printing techniques because of their low cost and high printing quality and color capability [1]. In the thermal inkjet printer, a thin film type heating resistor which converts electrical energy into thermal energy is generally used to eject the ink. These heating resistor materials should have a near-zero temperature coefficient of resistance (TCR) [2] for a stable ink ejection, a sufficient resistivity (>150 μΩ·cm) for making heating resistor of controllable thicknesses [3], and a high thermal stability due to its high operation temperature [4]. Since, however, 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 [5], only limited materials such as TaAl, HfB_2, and $TaN_{0.8}$ have been used as a heating resistor material [2, 5, 6].

Recently, it was reported that atomic layer deposited RuO_2–TiO_2 has many attractive hybrid functions for using it as a heating resistor such as adequate resistivity range with sufficiently low TCR values and high oxidation resistance even at high temperatures [4]. Moreover, it was shown that RuO_2–TiO_2 thin film resistor can be potentially used as a non-passivated type TIJ printhead where SiC or SiN passivation layers were eliminated. However, its corrosion resistance was not reported, though the corrosion resistance of the heating resistor is a very important property for the practical performance of heating resistor.

In this study, we investigated RuO_2–Al_2O_3 thin film resistor prepared by atomic layer deposition method to further improve the heating resistor properties. And, anticorrosion behavior was investigated in detail. Similar to TiO_2, Al_2O_3 is also an insulating material and has good oxygen diffusion barrier properties [7]. Compared to TiO_2, it can act as a moisture barrier [7] and has a stable amorphous structure up to 1,000 °C [8], which means that the use of Al_2O_3 could further improve the corrosion resistance.

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Experiment

RuO_2–Al_2O_3 thin films were deposited on 1,300 nm-thick SiO_2 formed on Si (100) substrates at a deposition temperature of 230 °C and at a deposition pressure of 3 Torr by atomic layer deposition adopting a super-cycle concept [9] for precise composition control. Bis(ethylcyclopentadienyl)-ruthenium [$Ru(EtCp)_2$, $Ru(C_2H_5C_5H_4)_2$] and trimethyl aluminum [TMA, $Al(CH_3)_3$] were used as precursors, and O_2 gas and O_2 plasma were used as a reactant for RuO_2 and Al_2O_3, respectively. $Ru(EtCp)_2$ and TMA were heated at 30 °C and 50 °C, respectively. The precursors were delivered to the reactor with Ar carrier gas at a flow rate of 50 sccm. One super-cycle for deposition of RuO_2–Al_2O_3 thin films consisted of two groups of subcycle dedicated for RuO_2 and Al_2O_3, respectively. Also, a subcycle consisted of several unit cycles, and in a unit cycle, four consecutive pulses were supplied. A unit cycle for Al_2O_3 was composed of TMA vapor pulse with 50 sccm Ar carrier gas, a purge pulse with 50 sccm Ar, O_2 plasma pulse with 120 sccm, and another 50 sccm Ar purge pulse; and a unit-cycle for RuO_2 was composed of a $Ru(EtCp)_2$ vapor pulse with 50 sccm Ar carrier gas, a purge pulse with 50 sccm Ar, a O_2 pulse with 120 sccm, and another 50 sccm Ar purge pulse. Table 1 summarized the supercycle design for atomic layer deposition (ALD) RuO_2–Al_2O_3 thin films. The six samples of RuO_2–Al_2O_3 thin films were prepared and labeled as A: $(RuO_2)_{0.16}$–$(Al_2O_3)_{0.84}$, B: $(RuO_2)_{0.29}$–$(Al_2O_3)_{0.71}$, C: $(RuO_2)_{0.43}$–$(Al_2O_3)_{0.57}$, D: $(RuO_2)_{0.58}$–$(Al_2O_3)_{0.42}$, E: $(RuO_2)_{0.66}$–$(Al_2O_3)_{0.34}$, F: $(RuO_2)_{0.72}$–$(Al_2O_3)_{0.28}$ films, and G: $(RuO_2)_{0.83}$–$(Al_2O_3)_{0.17}$, respectively. In the table, the letters a and b denote the number of unit cycles in RuO_2 and Al_2O_3 subcycles, respectively. These samples were prepared by adopting an adequate super-cycle for RuO_2–Al_2O_3 ALD, which is composed of RuO_2 and Al_2O_3 subcycle

The film thickness was measured with field emission scanning electron microscopy (FESEM; Hitachi, S-4800, Japan), and the film composition was analyzed using 9.0 MeV He^{2+} Rutherford backscattering spectroscopy (NEC, 3SDH, USA) and Auger electron spectroscopy (Perkin Elmer, SAM 4300, USA). The microstructures of the films were detected with an X-ray diffractometer (XRD; Rigaku, D/MAX-RC, Japan). And, the thickness and morphology of deposited films were analyzed using FESEM (Hitachi, S-4800, Japan). For evaluating the electrical characteristics, the sheet resistance of the films was measured through a four-point probe test. To evaluate the TCR properties of the films, sputtered aluminum electrode(100 nm) was patterned on the RuO_2–Al_2O_3 (100 nm)//SiO_2 (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 °C to 175 °C in a thermostatically controlled oven using a digital multimeter (HP3457A, Hewlett-Packard, USA). To evaluate corrosion resistance, electrochemical measurements (CMS 100, Gamry Instrument, USA) were performed in the typical three-electrode setup with a silver silver chloride electrode (SSCE, Ag/AgCl) as a reference electrode, a platinum counter electrode, and the coated sample as working electrode, connected to a potentiostat and a PC. Potentiostatic current density vs. time measurements were performed at a potential of 0.08 V vs. a SSCE in a 3 wt.% NaCl solution.

Results and discussion

Figure 1 shows the resistivities of the 100 nm thick RuO_2–Al_2O_3 thin films with respect to the RuO_2 intermixing ratio. At RuO_2 intermixing ratios less than 0.43, the film resistivity was increased drastically with decreases in the RuO_2 intermixing ratio. At RuO_2–Al_2O_3 thin films with RuO_2 intermixing ratios over 0.43, however, film resistivity did not undergo a steeper rate of change with increasing RuO_2 intermixing ratio. For RuO_2 intermixing ratios in the range 0.43–0.83, the resistivity of the films can be changed from 1,200 to 243 μΩ·cm, corresponding to appropriate resistivities for heating resistor application. The behavior of the film resistivities is very similar to that of RuO_2–TiO_2, in which

Table 1 Summary of super-cycle design for the preparation of RuO_2–Al_2O_3 thin films

Samples (a, b)	Number of unit cycles allocated to each subcycle		Film compositions
	Al_2O_3 (TMA–O_2 plasma)	RuO_2 ($Ru(EtCp)_2$ – O_2)	
A (1, 1)	1	1	$(RuO_2)_{0.16}$–$(Al_2O_3)_{0.84}$
B (1,15)	1	15	$(RuO_2)_{0.29}$–$(Al_2O_3)_{0.71}$
C (1,25)	1	25	$(RuO_2)_{0.43}$–$(Al_2O_3)_{0.57}$
D (1,30)	1	30	$(RuO_2)_{0.58}$–$(Al_2O_3)_{0.42}$
E (1,35)	1	35	$(RuO_2)_{0.66}$–$(Al_2O_3)_{0.34}$
F (1,40)	1	40	$(RuO_2)_{0.72}$–$(Al_2O_3)_{0.28}$
F (1,45)	1	45	$(RuO_2)_{0.83}$–$(Al_2O_3)_{0.17}$

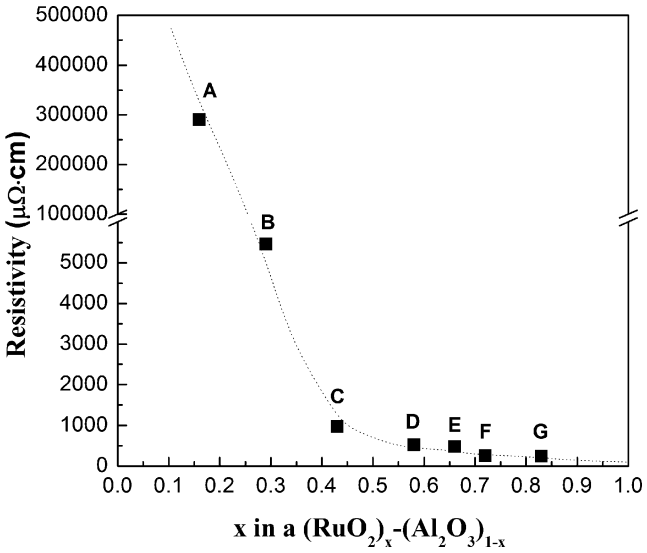

Fig. 1 The resistivity of RuO_2–Al_2O_3 thin films as a function of the RuO_2 intermixing ratio

the resistivities are initially very high due to the high contents of highly resistive TiO_2 and decrease gradually as the intermixing ratio of conductive oxide RuO_2 increases [6].

Figure 2 shows the TCR characteristics of as-deposited 100 nm thick RuO_2–Al_2O_3 thin films. At RuO_2 intermixing ratios of less than 0.43, the TCR values of the films decreased drastically up to −3,620 ppm/K (sample A). These TCR values are far too low to allow the use of these films in heating resistors. For the heater application, the magnitude of TCR values of the films should be minimized. At RuO_2 intermixing ratios exceeding 0.43, however, the TCR value slowly changed from −381 ppm/K (sample D) to −62.3 ppm/K (sample G). With appropriate intermixing ratios (samples E, F, and G), the RuO_2–Al_2O_3 thin films showed lower absolute values of TCR values than $TaN_{0.8}$(336 ppm/K). Though these TCR values were below that of pure RuO_2 film, they were within the range suitable for heating resistor applications. It seems to be due to the main composition of matrix changes from conductive RuO_2 to insulating Al_2O_3, similar to our previous results [4].

Figure 3 shows the effect of O_2 annealing on the TCR values of 100 nm thick RuO_2–Al_2O_3 films. For all specimens, the O_2 annealing time was fixed at 30 min. The results of TaN were obtained from our previous results [6] for comparison. As shown in Fig. 3, the TCR values of TaN decreased abruptly from 336 ppm/K to −3,800 ppm/K with increasing O_2 annealing temperature. However, the TCR values of RuO_2–Al_2O_3 did not undergo an abrupt change compared to TaN thin films and were maintained below 127 ppm/K even after annealing at 700 °C. From the XRD analysis (not shown here), the microstructure of RuO_2–Al_2O_3 was as-deposited amorphous and maintained as an amorphous after annealing 700 °C. Therefore, similar to the results of RuO_2–TiO_2 [4], it may be due to the retardation of crystallization as a result of the addition of Al_2O_3 to the RuO_2 matrix.

Figure 4 shows the SEM images of $(RuO_2)_{0.66}$–$(Al_2O_3)_{0.34}$ thin films before and after being immersed in aqua-regia at room temperature for 8 weeks. Before being immersed in aqua-regia, the surface of $(RuO_2)_{0.66}$–$(Al_2O_3)_{0.34}$ thin films were very smooth, and any defects such as pin-hole, cracks, or grain-boundaries were not observed. After being immersed in highly corrosive aqua-regia for 8 weeks, the surface of $(RuO_2)_{0.66}$–$(Al_2O_3)_{0.34}$ thin films can endure the corrosion and maintain a smooth surface. In order to investigate the detailed corrosion

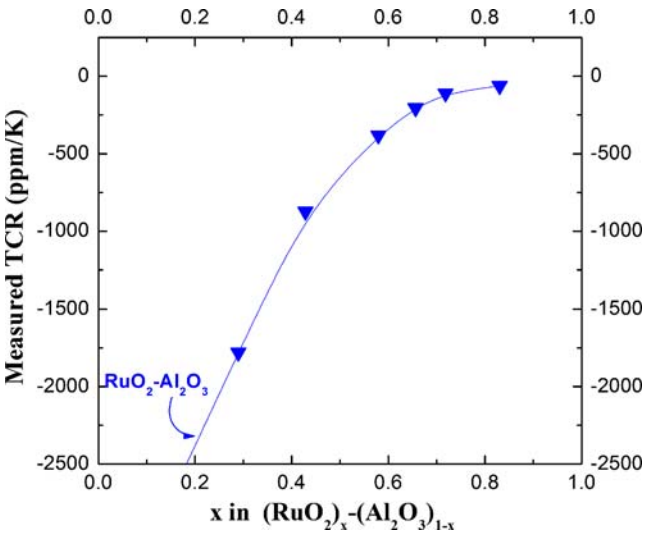

Fig. 2 Variation of TCR values of the RuO_2–Al_2O_3 thin films depending on RuO_2 intermixing ratios. Temperatures were varied from 25 °C to 175 °C

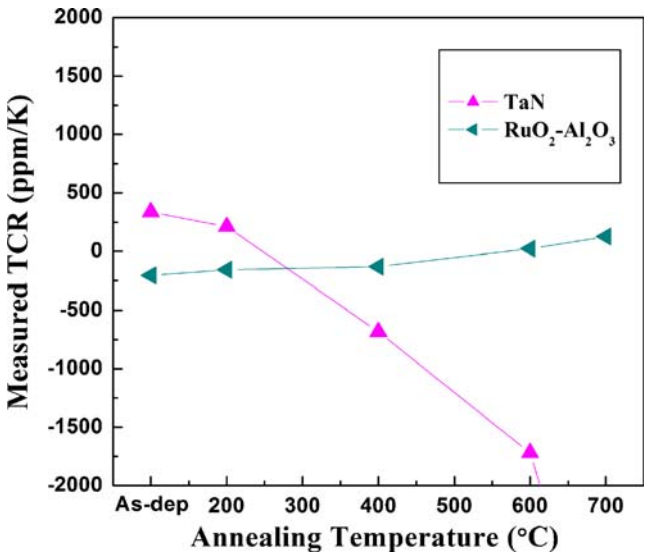

Fig. 3 The variation of TCR values of RuO_2–Al_2O_3 thin films depending on the O_2 annealing temperatures

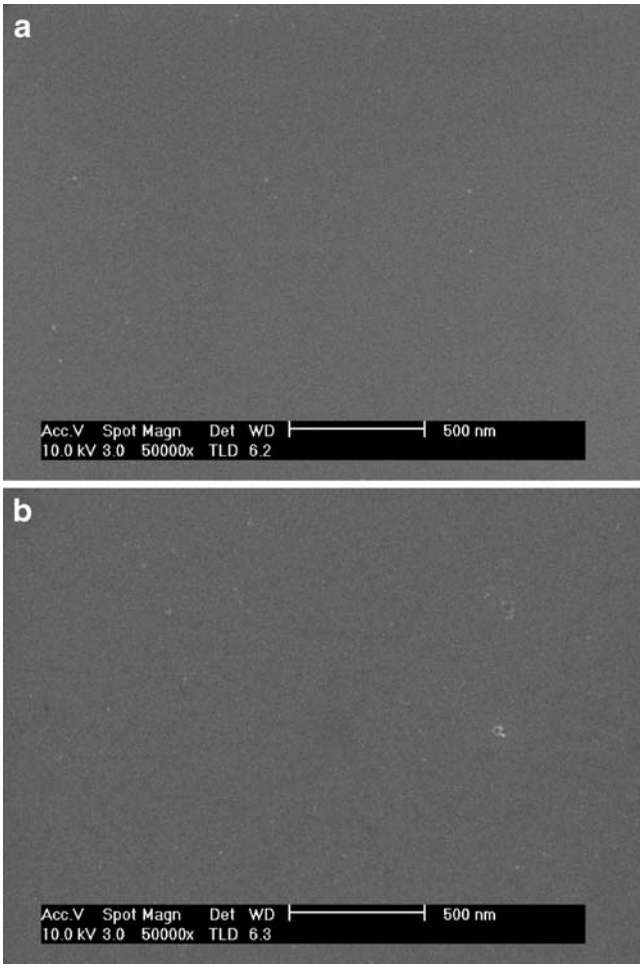

Fig. 4 The SEM images of $(RuO_2)_{0.66}$–$(Al_2O_3)_{0.34}$ thin films **a** before and **b** after being immersed in aqua-regia at room temperature for 8 weeks

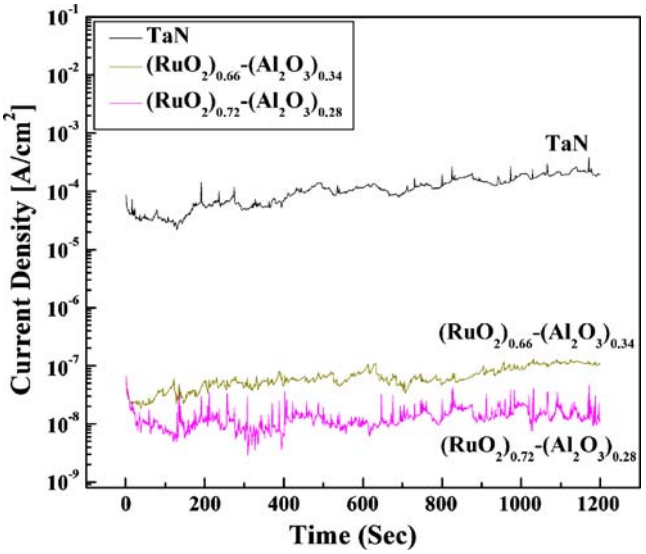

Fig. 5 Potentiostatic current density vs. time of TaN and various RuO_2–Al_2O_3 thin films

resistance of various $(RuO_2)_x$–$(Al_2O_3)_{1-x}$ thin film, potentiostatic current density of $(RuO_2)_{0.66}$–$(Al_2O_3)_{0.34}$ thin film were investigated as shown in Fig. 5. The potentiostatic current density measurement was carried out at a *potential* of +0.08 V vs. SSCE in 3 wt.% NaCl solution. As shown in Fig. 5, TaN coating showed high current density of 10^{-5} A/cm^2. As expected, the current density of $(RuO_2)_x$–$(Al_2O_3)_{1-x}$ thin films showed a lower current density in the range from 10^{-7} to 10^{-8} A/cm^2. Since both RuO2 and Al_2O_3 have a high corrosion resistance, it was conceivable that the RuO_2–Al_2O_3 thin films had a higher corrosion resistance. It can be also thought that the microstructure of RuO_2–Al_2O_3 thin films contributed the lower current densities because its microstructure is amorphous, which is favorable microstructure because it does not have grain boundaries. Thus, RuO_2–Al_2O_3 thin films showed hybrid functions such as sufficient TCR and resistivity, high oxidation resistance, and high corrosion resistance. It is particularly noteworthy that the previous and current results provide clues to engineer the resistivity and TCR value of materials for the application of heating resistors, i.e, conductive metal oxides, such as RuO_2, IrO_2, PdO_2, or OsO_2, have grain-size-dependent TCR characteristics with a low resistivity [4]. Therefore, the adjustment of resistivity as well as the improvement of TCR characteristics at high temperature can be achieved by intermixing ratios of insulating materials such as TiO_2, Al_2O_3, or SiO_2. In addition, its stable oxide form can provide a sufficient oxidation resistance. To obtain a sufficient corrosion resistance, an engineer can consider adequate conductive and insulating oxide having highly corrosion-resistive properties.

Conclusions

In summary, the hybrid functional RuO_2–Al_2O_3 thin films with low TCR values and appropriate resistivity range for heating resistor applications were presented by controlling the intermixing ratios. The TCR values of the RuO_2–Al_2O_3 thin films were maintained at −381 to −62.3 ppm/K by varying the RuO_2 intermixing ratios from 0.43 to 0.83, with resistivities remaining in the range of 1,200 to 243 μΩ·cm. Moreover, the RuO_2–Al_2O_3 thin films showed minimal change in TCR values even after O_2 annealing process at 700 °C. Due to higher corrosion resistance of both RuO_2 and Al_2O_3, the RuO_2–Al_2O_3 thin films had a high corrosion resistance. Therefore, hybrid functional RuO_2–TiO_2 thin films can serve as a suitable heating resistor material for non-passivated thermal inkjet printhead applications.

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