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Description	

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Preparation of Ruthenium Metal and Ruthenium Oxide Thin Films by a Low-Temperature Solution Process

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ABSTRACT

Highly conductive ruthenium metal thin films and ruthenium oxide ones were prepared by a solution process at low temperature (e.g., 6.9 × 10^{-5} Ωcm at 300°C for Ru^0). Their structure and electric properties depend on the annealing conditions. The process allowed us to fabricate ruthenium electrodes on flexible substrates.

1. INTRODUCTION

In organic thin film transistors (OTFTs), the properties of the interface between the source/drain (S/D) electrode and the semiconductor are critical for TFT performance. In recent years, gold (Au) has been the most widely used S/D electrode because of its high work function (5.0 eV). However, Au is expensive and difficult to pattern by etching. Therefore, many groups have studied alternative materials for S/D electrodes.[1]

Metal ruthenium (Ru^0) and ruthenium oxide (RuO_2) are attractive candidates owing to their high work functions (4.6 and 5.0 eV, respectively).[1] Furthermore, Ru^0 and RuO_2 have relatively low bulk resistivities (7.1 × 10^{-6} and 4.0 × 10^{-5} Ωcm, respectively) and high stability. In addition, they are good atomic diffusion barriers and are easy to etch.[2, 3]

The most commonly used routes for fabrication of Ru^0 and RuO_2 thin films have been sputtering and chemical vapor deposition.[1,2] However, these vacuum-deposition methods require expensive equipment, and therefore the manufacturing costs are high. As an alternative method, solution processes have various advantages including low processing temperatures, the ability to fabricate films with large areas, and relatively low cost.[4] However, the preparation of high-quality films by means of conventional solution processes commonly requires high annealing temperatures to decompose the organic additives and to crystallize the films. Though there have been several reports on the use of solution processes to prepare RuO_2 films, problems with low film quality and long processing time remain, [5] and there have been no reports on the use of solution processes for Ru^0 films.

In this paper, we report the fabrication of Ru^0 and RuO_2 thin films with low resistivity and low surface roughness by means of a solution process using a new precursor solution. By investigating the annealing conditions, we confirmed that nitrogen annealing effectively improved film performance. We obtained Ru^0 films with resistivities of 2.1 × 10^{-5} and 6.9 × 10^{-5} Ωcm when the process was carried out at 500 °C for 10 min and 300 °C for 30 min, respectively, under a nitrogen atmosphere. On the basis of these results, we fabricated a Ru^0 thin film on a polyimide (PI) substrate.

2. EXPERIMENTAL

Ruthenium(III) nitrosylacetate ($Ru(NO)(OAc)_3$; 99.99%, Alfa Aesar), 2-aminoethanol (MEA; 99%, Kanto Chemical), and propionic acid (PrA; 99.3%, Kanto Chemical) were used as received without further purification. $Ru(NO)(OAc)_3$ was dissolved in enough PrA and MEA to form a 0.35 M solution. The solution was stirred at 150 °C for 30 min under ambient conditions and then cooled to room temperature and filtered.

The Ru^0 and RuO_2 thin films were prepared from the precursor solution at various annealing temperatures and atmosphere conditions as follows. The precursor solution was spin-coated on a 500 nm-SiO_2/Si substrate at 2000 rpm for 25 s., and then the coated substrate was dried at 150 °C for 5 min to remove the solvent. The film was annealed in a rapid thermal annealing furnace (MILA-5000, ULVAC-RIKO).

The structures of the prepared thin films were characterized by means of X-ray diffraction (XRD; X'Pert PRO MRD, PANalytical), and the surface morphologies were investigated by means of atomic force microscopy (AFM; NanoNavi, SII) and scanning electron microscopy (SEM; S-4100, Hitachi). The electrical resistivity of the films was measured at room temperature by means of the four-point probe method (Loresta-EP with TFP probe, Mitsubishi Chemical Analytech). High-resolution transmission electron microscopy (HRTEM) was performed by the Kobelco Research Institute. Film thickness was evaluated by means of an electromechanical profiler (Alpha-Step, KLA-Tencor).

To fabricate a Ru thin film on a flexible substrate, we selected 125-μm-thick PI films (Kapton 500V, Du Pont-Toray), which have good stability at 300 °C.

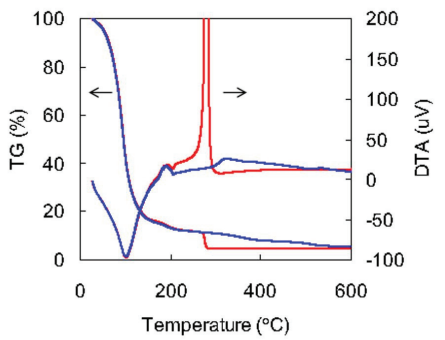

Fig. 1 Thermal analysis of the precursor solution under oxygen (red) and nitrogen (blue) atmospheres at a constant heating rate (10°C/min).

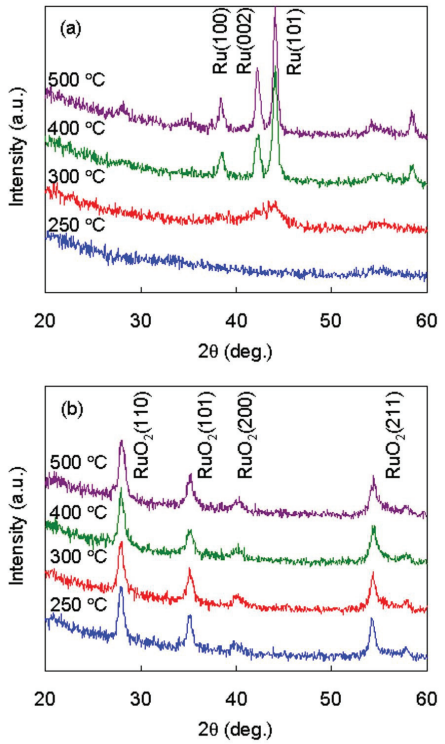

Fig. 2 XRD patterns of thin films prepared in (a) nitrogen and (b) oxygen at various annealing temperatures for 10 min.

3. RESULTS AND DISCUSSION

3.1 Thermal analysis of precursor solution

In the thermogravimetry–differential thermal analysis curves of the precursor solution measured at a constant heating rate (10 °C/min, Fig. 1), an endothermic peak due primarily to solvent evaporation was observed at 100 °C. When the analysis was conducted in oxygen, a sharp exothermic peak was observed at a 275 °C, indicating rapid pyrolysis of the Ru precursor. In contrast, the thermogravimetric curve of the solution measured in nitrogen showed a slow decrease from 300 °C. These results suggest that metal films or metal oxide films may have been formed at a temperature around 300 °C.

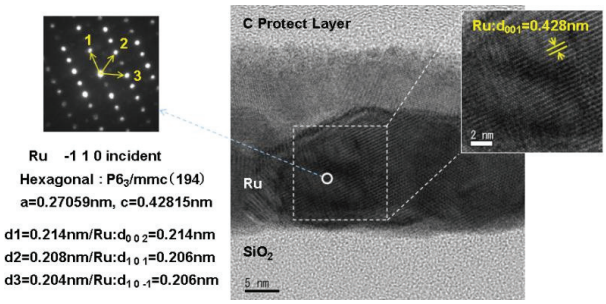

Fig. 3 HRTEM image and nano-beam diffraction pattern of Ru^0 thin films prepared in nitrogen at 500 °C.

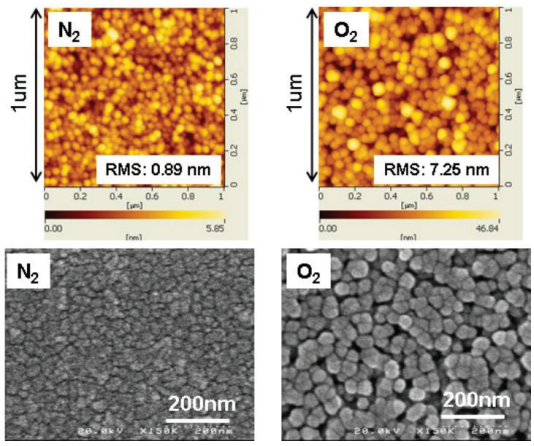

Fig. 4 AFM and SEM images of thin films prepared at 500 °C for 10 min under nitrogen and oxygen atmospheres.

3.2 Properties of Ru^0 and RuO_2 thin films

XRD analysis of the thin films annealed in nitrogen and oxygen at 250–500 °C revealed that the structure of the thin film depended on the annealing atmosphere (Fig. 2). Crystalline Ru^0 and RuO_2 were formed in nitrogen and oxygen, respectively. It is notable that Ru^0 thin films were formed in inert nitrogen in the absence of a reducing atmosphere (e.g., hydrogen). In our system, organic ligands, including the chelating MEA, must have acted as the reducing agent to form metallic Ru. The structure of the Ru^0 thin film formed in nitrogen at 500 °C was further analyzed by means of HRTEM (Fig. 3). Ru^0 crystals were directly observed (spacing of 0.428 nm for (001) planes) and were confirmed from electron diffraction.

The surface morphology of the films was studied by AFM and SEM (Fig. 4), which revealed that the films surface flatness after nitrogen annealing was much higher than that after oxygen annealing. The root mean square roughness values of the films annealed in nitrogen and oxygen were 0.89 and 7.25 nm, respectively.

We measured the resistivity of the thin films prepared from the precursor solution as a function of annealing temperature, time, and atmosphere (Fig. 5 and Table 1).

Table 1. Ru^0 and RuO_2 thin films prepared from the precursor solution under various conditions.

Temperature (°C)	Atmosphere	Time (min)	Thickness (nm)	Resistivity (Ωcm)
300	N_2	10	27	3.0×10^{-4}
300	N_2	30	26	6.9×10^{-5}
300	O_2	10	113	3.6×10^{-3}
300	O_2	30	112	2.7×10^{-3}
500	N_2	10	25	2.1×10^{-5}
500	O_2	10	43	3.0×10^{-4}
500	N_2/O_2 = 75/25	10	49	2.7×10^{-4}

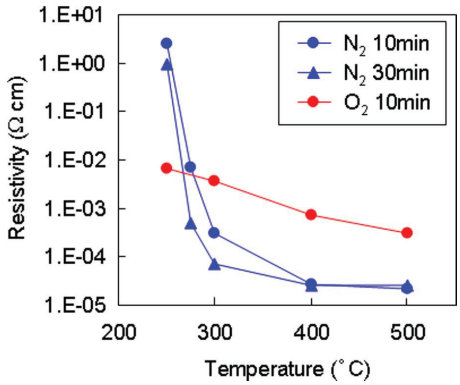

Fig. 5 Effect of annealing temperature, time and atmosphere on the resistivity of thin films prepared by a solution process.

The resistivity of an oxygen-annealed thin film decreased gradually with increasing annealing temperature. Under the nitrogen atmosphere, the resistivity decreased rapidly at 300 °C. The resistivities of the thin films prepared at 500 °C for 10 min under nitrogen and oxygen were 2.1×10^{-5} and 3.0×10^{-4} Ωcm, respectively; that is, the resistivity after nitrogen annealing was much lower than that after oxygen annealing. The conductivity of these films was superior to that of previously reported solution-processed RuO_2 thin films (4.15×10^{-4} Ωcm)[5] and similar to that of vacuum-processed Ru^0 and RuO_2 thin films (1.9×10^{-5} and 3.5×10^{-4} Ωcm, respectively).[1, 2] The very small thickness (~30 nm, Table 1) with such high conductivity indicates the high quality of the films.

In addition, the XRD patterns of the nitrogen annealed films showed temperature dependence corresponding to the resistivity. At 300 °C, at which temperature the resistivity rapidly decreased, the XRD pattern showed a broad peak at the positions of Ru^0 (002) and (101), indicating that the crystallization of Ru^0 started under these conditions. When the annealing temperature was increased, sharp diffraction lines indicating crystalline Ru were observed.

3.3 Fabrication of Ru^0 thin film on flexible substrate

To take the advantage of our low-temperature solution process, we fabricated Ru^0 thin films on a PI substrate. PI is thermally unstable above 350 °C, and thus the annealing temperature had to be below this temperature,

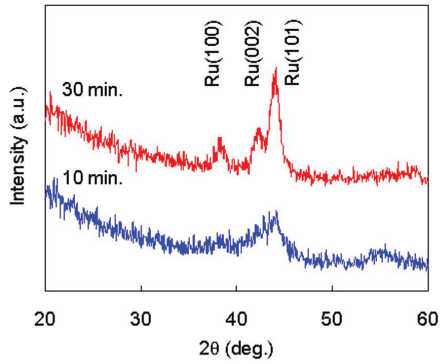

Fig. 6 XRD patterns of Ru^0 thin films prepared in nitrogen at 300 °C for 10 and 30 min.

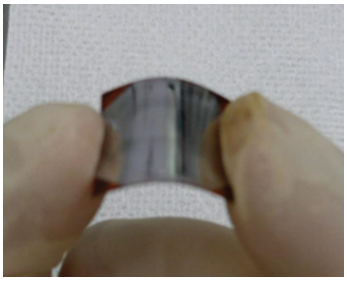

Fig. 7 Photograph of a Ru^0 thin film on a PI substrate.

and preferably below 300 °C. A crystalline Ru^0 thin film having high conductivity (6.9×10^{-5} Ωcm) was prepared at 300 °C for 30 min. In the XRD patterns of Ru^0 thin films prepared at 300 °C for 10 and 30 min (Fig. 6), sharp diffraction lines were observed under the extended annealing time, indicating the formation of crystalline Ru^0. Accordingly, we fabricated a Ru^0 thin film on a PI substrate (Fig. 7); the prepared film had metallic luster and conductivity.

4. CONCLUSION

We prepared highly conductive Ru^0 and RuO_2 thin films at low temperatures (300–500 °C) from a new precursor solution. The resistivities of films prepared under a nitrogen atmosphere at 500 °C for 10 min and at 300 °C for 30 min were 2.1×10^{-5} and 6.9×10^{-5} Ωcm, respectively. Furthermore, this is the first report of the preparation of crystalline Ru^0 thin film on a flexible substrate by means of a solution process. These results suggest the possibility of using solution-processed Ru electrodes for electronic devices (e.g., OLEDs).

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