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Highly conductive ruthenium oxide thin films by a low-temperature solution process and green laser annealing

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ABSTRACT

Highly conductive ruthenium oxide (RuO_2) thin films were prepared by a low-temperature solution process combined with green laser annealing (GLA). The process allowed production of RuO_2 films at a low temperature of 250 °C. GLA led to effective sintering of the film, significantly improving crystallinity and film density and resulting in joining between grains, and consequently, the conductivity was dramatically increased by one order or more. The RuO_2 thin films show a low resistivity (e.g., 7.6×10^{-5} Ω cm for a 40 nm-thick film), which was approximately 2 times of that of the single crystal RuO_2. Such resistivity has not been achieved only by thermal annealing, even at a high temperature of 800 °C, after solution deposition, and is similar or lower to that of vacuum-deposited RuO_2 films.

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1. Introduction

Ruthenium oxide (RuO_2) is an attractive candidate material for electrodes in memory devices and transistors owing to its relatively low resistivity (3.6×10^{-5} Ω cm for single crystal) [1] and high stability, as well as its high work function (~5 eV) and good susceptibility to dry etching. In our study on printed oxide electronics, RuO_2 has turned out to be an excellent printable material with both high conductivity and high chemical stability that can be processed in an ambient atmosphere [2]. In the study, we investigated a variety of conductive materials for our newly developed printing method (nano-rheology printing or nRP) [2], and found that the common conductors suffer various problems. For example, Cu suffers from oxidation during processing of subsequent oxide layers in air, Ag has a low interface adhesion to adjacent oxide layers, Al cannot be produced by a printable precursor, and Pt still cannot be patterned by nRP.

The most commonly used routes for the fabrication of RuO_2 thin films have been sputtering [3,4], chemical vapor deposition [5,6], and atomic layer deposition [7,8]. 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 fast processing, simple and low-cost equipment, the ability to fabricate films with large areas, and applicability to printed electronics [2]. Despite the benefits of low cost and fast processing, the solution preparation of high-quality RuO_2 films has gained little progress in the last decade [9,10]. Very recently, we have developed an amine-complex-based solution process that enables nRP patterning of RuO_2 [11]. These processes commonly require high annealing temperatures over 400 °C to decompose the precursors and to densify the films. Even so, the effect in reducing resistivity is small by thermal annealing (e.g., from 3.1×10^{-4} Ω cm at 400 °C decreased to 1.8×10^{-4} Ω cm at 800 °C) [10] because RuO_2 is highly thermally stable and the densification via solid diffusion in conventional heating is very slow. In addition, the high annealing temperature can cause damages of other parts (e.g., plastic substrates and silicon circuits) during device fabrication.

In laser annealing, the sample surface or film can be locally heated to a temperature high enough for fast sintering while the bulk of the sample or the substrate (e.g., a polymer substrate) maintains at a low temperature. The excimer laser annealing (ELA) process has been utilized to achieve a low-temperature process of silicon and metal oxide transistors [12]. As an alternative of laser annealing, green laser annealing (GLA), which uses all-solid-state laser, is an attractive candidate owing to its low maintenance cost, stable laser power and a large process window [13]. There have been several reports on the utilization of GLA technique for metal oxides [14]. For solution processing of RuO_2, use of laser irradiation to decompose the dried (below 100 °C) precursor films into RuO_2

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films has been reported [15], but the resultant films had resistivity values ($\sim 4\times10^{-3}\ \Omega$ cm) similar to those of typical thermally decomposed ones at low temperatures (below 300 °C), indicating the laser irradiation did not resulted in sintering of the films.

The solution process we developed allows low-temperature preparation (below 300 °C) of RuO_2 films [11]. In this paper, we report applying green laser to the RuO_2 films produced by this process to effectively sinter them into 50% denser ones with a low resistivity of $7.6\times10^{-5}\ \Omega$ cm.

2. Experimental procedure

Ruthenium(III) nitrosylacetate ($Ru(NO)(OAc)_3$, Alfa Aesar), Monoethanolamine (MEA, Kanto Chemical), and propionic acid (PrA, Kanto Chemical) were used as received without further purification. $Ru(NO)(OAc)_3$ was dissolved in enough PrA and MEA (molar ratio MEA/Ru=2) to form a 0.35 M solution. The solution was stirred at 150 °C for 30 min under the ambient atmosphere and then cooled to room temperature and filtered.

The precursor solution was spin-coated on a glass substrate (OA-10) 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 at 250 °C for 10 min under air. The films were irradiated with the green laser (515 nm) with a various energy densities (LAVA 100, Innovavent GmbH).

The light absorption properties of the prepared thin films were investigated by UV–vis spectrophotometer (V-630, JASCO). The structures and density of the prepared thin films were characterized by X-ray diffraction (XRD) and X-ray reflectivity (XRR) analyses (X'Pert PRO MRD, PANalytical), and the surface morphologies were investigated by scanning electron microscopy (SEM; S-4100, Hitachi). The electrical resistivity of the films was measured at room temperature by the four-point probe method (Loresta-EP with TFP probe, Mitsubishi Chemical Analytech). Film thickness was evaluated by an electromechanical profiler (Alpha-Step, KLA-Tencor).

3. Results and discussion

Light absorption spectra of the thin films from the precursor solution annealed at 100–500 °C in air were examined (Fig. 1a). The absorption of the films increased rapidly at 250 °C, which corresponds to the starting temperature of RuO_2 formation from the precursor films, as indicated by XRD analysis (Fig. 1b). Thermal analysis in our previous study showed that the organic components in the precursor decomposed at ~250 °C [11]. (Detailed analysis of the structure and decomposition behavior of such Ru-amine complexes will be reported in a full paper that is in finalizing now.) These results suggest that RuO_2 has stronger absorption in a wider range of wavelength than the precursor and that our GLA system having a laser wavelength of 515 nm may be utilized for RuO_2 thin films.

The RuO_2 thin films annealed at 250 °C were irradiated with a green laser under ambient conditions. XRD analysis of the RuO_2 thin films irradiated with a green laser revealed that the crystal structure of the films depended on the energy density of the green laser. When the energy density was increased, diffraction lines became more intense and sharper as shown in Fig. 2. The XRD pattern of the RuO_2 thin films before GLA shows a broad peaks at the positions of RuO_2 (110), (101) and (211). In contrast, sharp diffraction lines were observed after GLA. Because the measurement conditions for XRD were same, this indicates GLA significantly improved the crystallinity of the RuO_2 thin films.

The surface morphology of the RuO_2 thin films before and after GLA was studied by SEM (Fig. 3). The microstructure of the films before GLA showed small (~30 nm) granular crystallites. With increasing laser energy density in GLA, the crystallites grew larger (~100 nm), accompanying sintering between grains. The joining between crystallites as a result of sintering was clearly visible after GLA at 0.7 J/cm^2. The microstructure evolution with the laser energy density is consistent with the change in XRD patterns.

We measured the resistivity and thickness of these films (Fig. 4). The resistivity of the films decreased with increasing energy density of GLA. The resistivities of the films before and after GLA at 0.7 J/cm^2 were 1.4×10^{-3} and $7.6\times10^{-5}\ \Omega$ cm, respectively, with more than one order decrease after GLA. The conductivity of the films irradiated with GLA was similar or superior to that of previously reported

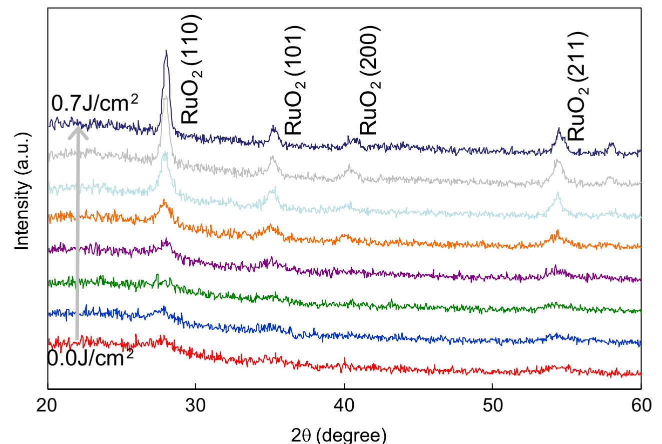

Fig. 2. XRD patterns for the RuO_2 thin films annealed at 250 °C after GLA as a function of energy density.

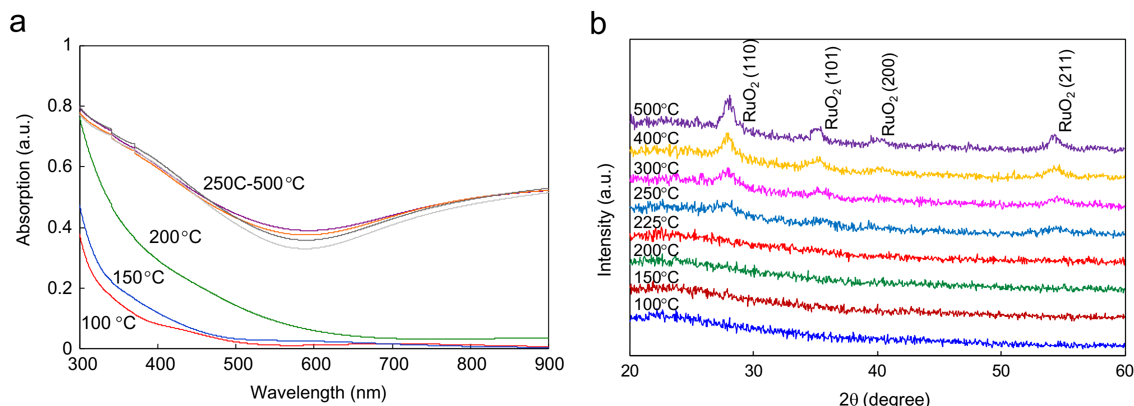

Fig. 1. Absorption spectra (a) and XPD patterns (b) of thin films prepared from the precursor solution and annealed in air at various temperatures for 10 min.

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