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Thermal solid-phase crystallization of amorphous CuCrO2:N thin films deposited by reactive radio-frequency magnetron sputtering

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A B S T R A C T

In order to fabricate highly-oriented delafossite $CuCrO_2$ (CCO) thin film which is one of the candidate materials for a p-type transparent conductive oxide, thermal solid-phase crystallization of an amorphous N-doped CCO (CCO:N) film was investigated. The amorphous CCO:N films were deposited at room temperature by reactive radio-frequency sputtering in an Ar/N_2 gas mixture atmosphere, and they were subsequently calcined in N_2. A N_2 partial pressure (α_{N2}) during the film deposition and a calcination temperature (T_C) were varied within the range from 0 to 90% and 500 to 900 °C, respectively. By the calcination at 550 °C and above, c-axis orientation was observed regardless of α_{N2}. Furthermore, at α_{N2} of 70 and 90%, a six-fold symmetry of $CuCrO_2$[110]//Al_2O_3[300] was confirmed at T_C of 800 °C and above. Average optical transmittance (λ = 450–800 nm) of the as-deposited CCO:N films was 45% and increased to 60% and over simultaneously with c-axis orientation. Resistivity of the calcined CCO:N film decreased with increasing T_C up to 600 °C but it rebounded drastically at T_C of 650 °C. This implies that resistivity was mainly affected by the number of intrinsic defects. From X-ray diffraction and X-ray photoelectron spectroscopy measurements, metal nitrides were formed in the as-deposited CCO:N film and it effectively acted to assist the generation of Cu^+ and $CuCrO_2$ bonds. N atoms were desorbed during the calcination but it was confirmed the initial formation of these desirable bonds effectively improved orientation of the delafossite structure.

1. Introduction

Transparent conducting oxides (TCOs) have been widely used for some semiconductor devices such as light-emitting diodes [1], smart windows [2], and solar cells [3]. A high-quality p-type TCO thin film is necessary for these devises, and the delafossite oxides such as $CuAlO_2$, $CuGaO_2$, and $CuCrO_2$ (CCO) are promising candidates [4]. ABO_2 delafossite oxides (space group $R\bar{3}m$ and $P6_3/mmc$) consist of alternate layers of monovalent A cation and octahedral BO_6 along the c-axis [5]. Among many delafossite oxides, the magnesium-doped CCO showed the lowest p-type resistivity of 4.5×10^{-3} Ωcm [6].

Although there are several reports on the methods for depositing the CCO films, for example, pulsed laser deposition [7,8], molecular beam epitaxy [9], sol-gel processing [10], chemical vapor deposition [11], and radio-frequency (RF) magnetron sputtering [6,12], crystallinity of the CCO films was not so good. Particularly, the in-plane crystalline orientation is one of the most important factors to form high quality heterostructures and prevent a deterioration in the device performance. Tilted orientations of CCO, for example, (012) and (101), are easily formed [13,14]. This undesired structure with defects at the heterojunction interface degraded the device performance. In addition, oxides, such as CuO and Cu_2O whose respective bandgaps are 1.5 and 2.1 eV [15,16], are easy to be formed as secondary phase into the CCO. Those precipitates decrease optical transmittance and deteriorate the optical properties, so it is necessary to develop the method for depositing a single oriented CCO without the precipitation formation.

For this purpose, we investigated the thermal solid phase crystallization (SPC) of an amorphous CCO film on a c-face sapphire [Al_2O_3(0001)] substrate. The c-face sapphire is suitable as the epitaxial substrate because the in-plane epitaxial relationship of $CuCrO_2$[110]//Al_2O_3[100] has low lattice mismatch of about 8.3%. In our previous study, we reported that N_2 addition in the Ar sputtering gas was effective to suppress the CuO precipitation and promote the formation of O-Cu-O dumbbell bonds in the delafossite structure [17]. Thereby, combination of the SPC and the N doping has a possibility to obtain a highly-oriented CCO film.

2. Film preparation and evaluation

The amorphous CCO or N-doped CCO (CCO:N) thin film was

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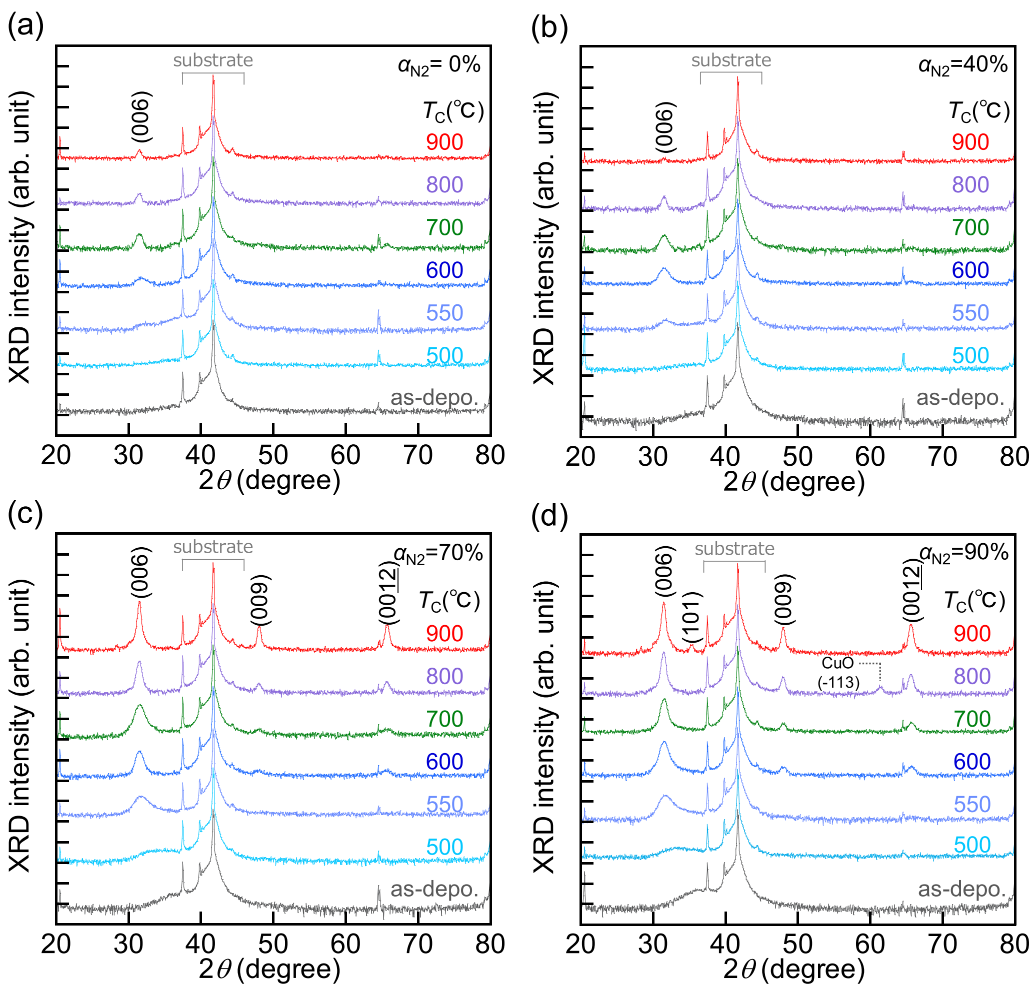

Fig. 1. Out-of-plane XRD patterns of the as-deposited films and the films calcined at 500 to 900 °C. α_{N2} is (a) 0%, (b) 40%, (c) 70%, and (d) 90%.

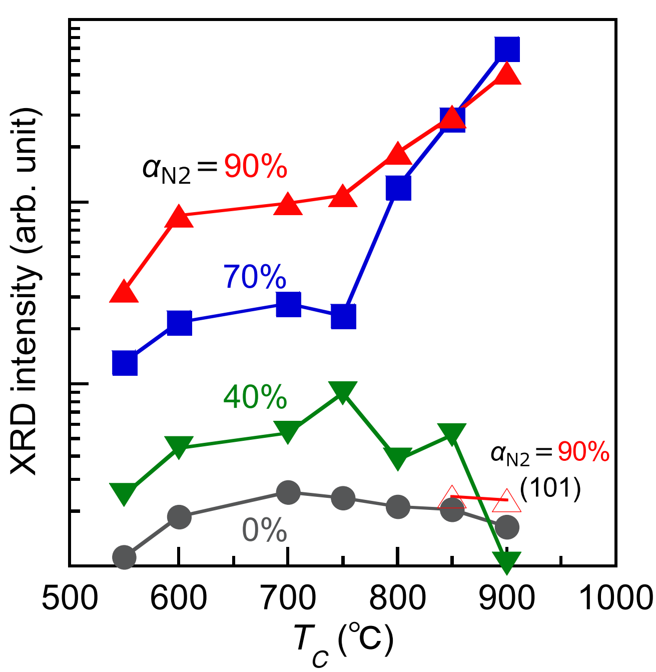

Fig. 2. Dependence of XRD intensity on T_C.

deposited on the c-face sapphire substrate at room temperature by reactive RF magnetron sputtering using a stoichiometric ceramic CCO target (purity: 99.9%). The target diameter and the distance between the target and the substrate were 80 mmϕ and 110 mm, respectively. The total pressure of the Ar/N_2 sputtering gas was 1.0 Pa. The ratio of the N_2 partial pressure (P_{N2}) to the total pressure (P_{Ar} + P_{N2}), here denotes as α_{N2}, was varied within the range from 0 to 90%. The RF power was 150 W. Film thickness was fixed to 50 nm by adjusting a sputtering duration according to the growth rate, and it was confirmed by the stylus profiler (Kosaka Laboratory Ltd. ST4000M). The film composition was evaluated by X-ray fluorescence (XRF, Rigaku RIX 2100) measurement by using the ceramic target as a stoichiometric reference. The formed CCO film was slightly Cu rich (The typical atomic ratio of Cu to Cr was about 1.1.).

The amorphous films were thermally calcined by lamp heating under N_2 atmosphere of 1000 Pa for 5 min. The calcination temperature (T_C) was varied in the range of 500 to 900 °C. The crystal structure was evaluated by non-monochromated X-ray diffraction (XRD, Rigaku SmartLab) to observe the weak diffraction peaks from the precipitated oxides such as CuO and Cu_2O. The X-ray of XRD measurement was generated by an electron tube with a Cu target and a W filament, and operating voltage and current were 40 kV and 30 mA. The optical transparency was measured by spectroscopic ellipsometry (J.A. Woollam Co. M-2000). The electrical resistivity and the chemical binding states of adatoms were measured by van der Pauw method and X-ray photoelectron spectroscopy (XPS, Kratos AXIS-Nova), respectively. The photoelectron was generated with monochromatic Al-K_α X-ray source using voltage of 15 kV and current of 18 mA. The binding energy was calibrated using adventitious C 1s at 284.6 eV as a