Journal of Crystal Growth 311 (2009) 1117–1122

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Optical and electrical properties of $CuScO_2$ epitaxial films prepared by combining two-step deposition and post-annealing techniques

Yoshiharu Kakehi [a,*], Kazuo Satoh [a], Tsutom Yotsuya [a], Keiichiro Masuko [b], Takeshi Yoshimura [b], Atsushi Ashida [b], Norifumi Fujimura [b]

[a] Technology Research Institute of Osaka Prefecture, 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan
[b] Department of Physics and Electronics, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai 599-8531, Japan

ARTICLE INFO

Article history:
Received 25 July 2008
Received in revised form
16 November 2008
Accepted 17 November 2008
Communicated by D.P. Norton
Available online 21 November 2008

PACS:
81.15.Fg
81.15.Np
73.61.Le

Keywords:
A1. Characterization
A3. Laser epitaxy
B1. Oxides
B2. Semiconducting ternary compounds

ABSTRACT

A $CuScO_2$(0 0 0 1) epitaxial film with a thickness of a few hundred nanometers was successfully grown on an *a*-plane sapphire substrate by combining the two-step deposition and post-annealing techniques. The film was single-phase with a rhombohedral crystal structure and showed six-fold rotational symmetry in the basal plane, indicating that the film had a twinned domain structure. The orientation relationships of the film with respect to the substrate were $CuScO_2$[3R](0 0 0 1)//sapphire(1 1 $\bar{2}$ 0) and $CuScO_2$[3R][1 1 $\bar{2}$ 0]//sapphire[0 0 0 1]. The average optical transmittance of the film was higher than 60% in the visible/near-infrared regions, and the energy gap for direct allowed transition was estimated to be 3.7 eV. The p-type conduction of the film was confirmed by Hall measurement. The electrical conductivity, carrier concentration, Hall mobility, and Seebeck coefficient of the film at room temperature were $1.0\times10^{-3}\,S\,cm^{-1}$, $4.5\times10^{16}\,cm^{-3}$, $1.4\times10^{-1}\,cm^2\,V^{-1}\,s^{-1}$, and $+968\,\mu V\,K^{-1}$, respectively. The activation energy estimated from the temperature dependence of the carrier concentration was 0.62 eV.

1. Introduction

In recent decades, p-type transparent semiconductors, such as Cu^+-based oxides [1–8], oxychalcogenides [9], and chalcogenide fluorides [7,10], have attracted much attention due to the potential optoelectronic applications based on transparent p–n junctions.

Copper-scandium oxide (CSO) is a p-type transparent Cu^+-based delafossite. In Cu^+-based delafossites, holes can be introduced either by substituting divalent species for the octahedral trivalent cation sites or by intercalating with excess oxygen near the Cu^+ planes [11,12]. The Cu–Cu distances also significantly influence the Cu–Cu interactions, i.e., electrical conductivity, because holes predominantly pass through the Cu^+ planes [11–13]. Holes in CSO can be induced by substituting divalent species for Sc sites [7,8,12]. CSO is a Cu^+-based delafossite with the smallest Cu–Cu distance for which excess oxygen intercalation is possible [11,12]. Therefore, CSO potentially has the highest p-type electrical conductivity in transparent Cu^+-based delafossites.

CSO has two crystalline phases depending on the stacking periods along the *c*-axis: rhombohedral (CSO[3R]) and hexagonal (CSO[2H]) [11,12]. The *a*-axis lattice constants of each phase are 0.3216 nm for CSO[3R] and 0.3215 nm for CSO[2H], which are larger than that of a p-type transparent $CuAlO_2$ (0.2857 nm). They are very close to that of ZnO (0.3249 nm) and the misfit of the *a*-axis lattice constant between CSO and ZnO is about 1%. ZnO is a typical n-type transparent conducting oxide and has a hexagonal crystalline structure. Therefore, transparent p–n heterojunctions with excellent interfaces are possible to be fabricated with CSO(0 0 0 1)/ZnO(0 0 0 1) epitaxial films.

We reported on the epitaxial growth of CSO[3R] thin films with a 50-nm thickness prepared at relatively low deposition rates by a pulsed laser deposition (PLD) method [14,15]. However, it was possible to easily grow grains with different orientations and other phases in CSO thin films by increasing the film thickness using a long deposition time or a high laser repetition frequency [16]. We also reported that the out-of-plane orientation, crystallinity along both out-of-plane and in-plane directions, and surface morphology of CSO[3R] polycrystalline films deposited at relatively high deposition rates were significantly improved by the post-annealing treatment, and that highly *c*-axis-oriented CSO[3R] films a few hundred nanometers thick were fabricated by post-annealing CSO[3R] polycrystalline films at an optimal oxygen

*Corresponding author. Tel.: +81 725 51 2671; fax: +81 725 51 2639.
E-mail address: kakehi@tri.pref.osaka.jp (Y. Kakehi).

0022-0248/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2008.11.060

pressure [16]. However, the in-plane orientation of the films was hardly improved by the post-annealing treatment; thus, it was difficult to obtain thicker CSO(0 0 0 1) epitaxial films. Therefore, CSO thin films with the bilayered structure consisting of a polycrystalline layer a few hundred nanometers thick on a thin epitaxial layer were deposited on *a*-plane sapphire substrates to arrange the in-plane orientation of films in one direction, because it is well known that the orientation of a thin initial layer grown on a substrate has a significant influence on the orientation of the whole film [17–19]. As a result, p-type transparent CSO[3R](0 0 0 1) epitaxial films a few hundred nanometers thick were successfully prepared by post-annealing the films with the bilayered structure. The crystallinity along both out-of-plane and in-plane directions of the epitaxial films was significantly improved compared with that of the films with the bilayered structure.

In this paper, we report on the effect of laser fluence on the in-plane orientation of both layers (CSO(0 0 0 1) epitaxial layer and CSO polycrystalline layer) forming CSO thin films with the bilayered structure. The crystallographic, optical, and electrical properties of the films obtained by post-annealing the films with the bilayered structure are also discussed.

2. Experimental procedure

CSO thin films were deposited by a PLD apparatus with an oxygen radical source (ULVAC: MB95-5005) using a $Cu_2Sc_2O_5$ pellet as a target [14–16]. A KrF excimer laser beam (λ=248 nm, pulse duration=30 ns) was used for the ablation. The substrates were *a*-plane sapphire, because the sapphire *c*-axis lattice constant (1.2991 nm) matched the four-fold-longer constants of the CSO *a*-axis lattice constant with less than a 1.01% misfit. Therefore, it is presumed that CSO thin films are epitaxially grown on *a*-plane sapphire substrates based on the uniaxial-locked epitaxy mechanism [20]. Before deposition, the sapphire substrates were annealed in oxygen at 1150 °C to obtain atomically flat surfaces. The distance from the target and the substrate was 40 mm.

The crystallographic structure, crystallinity, and orientations along the out-of-plane and in-plane directions against the substrate were characterized with an X-ray diffractometer (XRD) using *Cu* $K\alpha_1$ radiation (PANalytical: X'pert PRO MRD). The optical transmission spectra were measured by a spectrophotometer (Shimadzu: UV-3100). The film thickness was determined using a surface profilometer (KLA Tencor: P-15). The electrical transport properties were measured by the van der Pauw method using an ac magnetic field modulation system from 300 to 373 K (TOYO, ResiTest 8310). Four Pt electrodes were deposited by ion beam sputtering and annealed at 773 K for 1 h under an oxygen pressure of 13 Pa to obtain ohmic contacts. The Seebeck coefficient was also measured at room temperature.

3. Results and discussion

3.1. Laser fluence effect on in-plane orientation of CSO thin films

It is very important for the preparation of thicker CSO(0 0 0 1) epitaxial films using the post-annealing treatment to arrange the in-plane orientation of the few-hundred-nanometer-thick CSO thin films with the bilayered structure in one direction. In this section, the laser fluence effect on the in-plane orientation of both layers forming CSO thin films with the bilayered structure is investigated.

First, CSO thin films were deposited on *a*-plane sapphire substrates at various laser fluences to obtain a thin CSO(0 0 0 1) epitaxial layer. With reference to our previous report [14], other deposition parameters were as follows: the substrate temperature was 925 °C, oxygen pressure was 1.5 Pa, the rf power of the oxygen radical source was 200 W, the laser repetition frequency was 1 Hz, and deposition time was 1–2 h.

Fig. 1 shows the XRD $2\theta/\omega$ patterns of CSO thin films deposited at various laser fluences. Diffraction peaks corresponding to CSO[3R] 0003, 0006, 0009, and 00012 were confirmed in all deposited films. Cu_2O 110, 111, and 220 peaks also appeared when the films were prepared at laser fluences ranging from 1.0 to 1.8 J cm^{-2}.

The in-plane orientation relationship between the substrate and the film was investigated by XRD ϕ-scan measurements. The results using $30\bar{3}0$ diffractions of the substrate and $10\bar{1}4$ diffractions of the CSO[3R] thin film are shown in Fig. 2. Sharp peaks with the two-fold symmetry were observed for $30\bar{3}0$ diffractions of the substrate, as shown in Fig. 2(a). On the other hand, peaks for $10\bar{1}4$ diffractions of the films prepared at a laser fluence of less than or equal to 1.0 J cm^{-2} exhibited six-fold symmetry, indicating that the films had twin structures (Fig. 2(b) and (c)). The peaks of the films were in agreement with those of the substrate at the ϕ diffraction angles of $\pm 90°$. Therefore, the in-plane orientation relationship for the film with respect to the substrate was CSO[3R][$11\bar{2}0$]// sapphire[0 0 0 1]. With increasing laser fluence, peaks corresponding to a new six-fold symmetry component appeared, which indicate the in-plane orientation relationship of CSO[3R][$11\bar{2}0$]// sapphire[$8\bar{8}01$] [14], as shown in Fig. 2(d) and (e). Only peaks with the in-plane orientation relationship of CSO[3R][$11\bar{2}0$]// sapphire[$8\bar{8}01$] were observed when the film was prepared at a laser fluence of 2.6 J cm^{-2} (Fig. 2(f)).

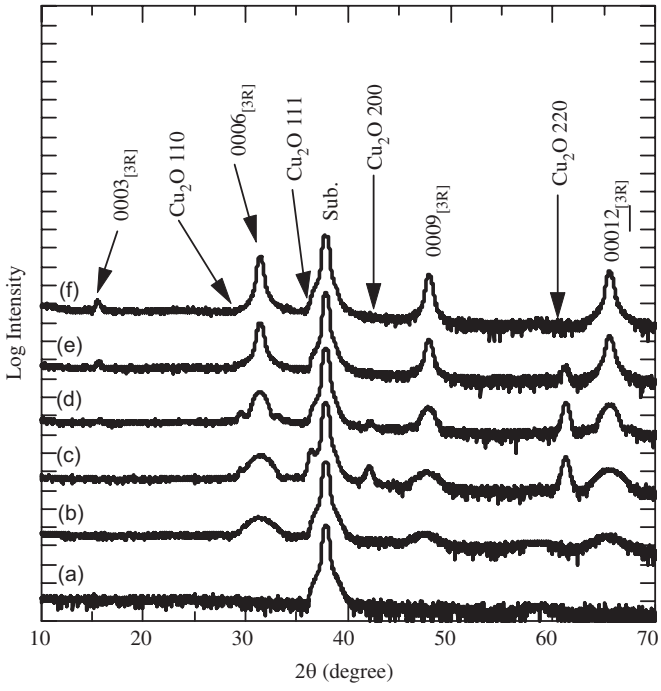

Fig. 1. XRD $2\theta/\omega$ patterns of CSO thin films deposited on *a*-plane sapphire substrates at various laser fluences. (a) substrate, (b) 0.6 J cm^{-2}, (c) 1.0 J cm^{-2}, (d) 1.1 J cm^{-2}, (e) 1.8 J cm^{-2}, and (f) 2.6 J cm^{-2}. Other deposition parameters were as follows: substrate temperature: 925 °C, oxygen pressure: 1.5 Pa, rf power of the oxygen radical source: 200 W, laser repetition frequency: 1 Hz, and deposition time: 1–2 h.