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Fabrication of β-$AgGaO_2$ thin films by radio frequency magnetron sputtering

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ABSTRACT

Thin films of β-$AgGaO_2$, were fabricated on (0001)–Al_2O_3 substrates by radio frequency magnetron sputtering. β-$AgGaO_2$ is a ternary oxide semiconductor possessing a wurtzite-derived β-$NaFaO_2$-type structure. The effects of changing experimental parameters including sputtering atmosphere, pressure and substrate temperature were investigated. The effects of the sputtering conditions on the composition, phase, morphology and optical transmission of the films were determined. A highly crystalline β-$AgGaO_2$ film was obtained by deposition at 200 °C under a 15% O_2 atmosphere at a pressure of 0.5 Pa. This film was (001)-oriented, similar to wurtzite-type phases. The energy band gap of β-$AgGaO_2$ was determined to be 2.2 eV from its photocurrent spectrum.

1. Introduction

The structure of β-$NaFeO_2$ is wurtzite-derived, in which monovalent and trivalent cations occupy the divalent cation site in the wurtzite-type oxide and the cations have an ordered arrangement, as shown in Fig. 1. The structural relationship between β-$NaFeO_2$ and wurtzite is similar to that between chalcopyrite-type I–III–VI_2 and zincblende-type II–VI semiconductors such as $CuInSe_2$ and CdSe, respectively. For example, β-$NaFeO_2$-type oxides such as β-$LiGaO_2$ [1], β-$LiAlO_2$ [2], β-$AgGaO_2$ [3–5] and β-$AgAlO_2$ [6,7] are ternary I–III–VI_2 oxide semiconductors with a diamond-related structure. These semiconductor materials are expected to show good potential for a variety of functions and applications.

Recently, we found that β-$LiGaO_2$ forms an alloy semiconductor with ZnO over a wide composition range because of their structural similarity, and the energy band gap of ZnO is widened up to 4.0 eV by alloying [8–12]. This is the first example of an oxide semiconductor that consists of a II–VI and I–III–VI_2 alloy system. In ZnO-based semiconductors, narrowing of the energy band gap is usually demonstrated by alloying with CdO [13–17]. However, the toxicity of cadmium means that ZnO–CdO alloys are not suitable for practical use. When the energy band gap of ZnO is reduced by alloying with a non-toxic β-$NaFeO_2$-type ternary oxide, the ZnO-based semiconductors become responsive to visible light. β-$AgGaO_2$ is a suitable material for this purpose because its energy band gap is 2.19 eV, [4] and its lattice mismatch with ZnO is small: 4.6% and 5.2% for the *ab*-plane and *c*-axis, respectively. In addition, in β-$AgGaO_2$, holes introduced into the valence band are expected to be delocalized because the Ag 4d orbitals should contribute substantially to the valence band. Therefore, β-$AgGaO_2$ is potentially a p-type oxide semiconductor, similar to Ag_2O and delafossite-type α-$AgGaO_2$ [18,19].

In the present study, we fabricated β-$AgGaO_2$ thin films by radio frequency (rf) magnetron sputtering. The effects of varying experimental conditions such as sputtering atmosphere, pressure and substrate temperature on the composition, phase, morphology and optical properties of the resulting films are investigated.

2. Experimental procedures

β-$AgGaO_2$ powder was used as a target in thin film fabrication, and was prepared by ion-exchange of Na^+ ions in a β-$NaGaO_2$ precursor for Ag^+ ions in a mixed molten salt, as reported previously [3,4]. The precursor β-$NaGaO_2$ was prepared by solid state reaction of Na_2CO_3 (99.8%; Wako Pure Chemical Industries, Japan) and Ga_2O_3 (99.99%; Kojundo Chemical Laboratory, Japan). Na_2CO_3 and Ga_2O_3 were weighed, mixed, and then pressed into disks with a diameter of 17.2 mm at 256 MPa. The disks were fired at 900 °C for 12 h. The disks were pulverized and then mixed with $AgNO_3$ (99.9%; Wako Pure Chemical Industries, Japan) and KNO_3 (99.9%; Wako Pure Chemical Industries, Japan) with a molar ratio of β-$NaGaO_2$:$AgNO_3$:KNO_3 of 1:1.2:1. The mixed powder was heated at 200 °C for 20 h, and then the resulting product was washed with ultrapure water. The obtained powder was dried at room temperature in a vacuum desiccator.

$AgGaO_2$ films were deposited on (0001)–Al_2O_3 single crystal substrates by conventional rf magnetron sputtering. β-$AgGaO_2$ targets were made by spreading the powder so that it covered the bottom of a 2-inch diameter aluminum plate. The effects of varying sputtering atmosphere, pressure and substrate temperature were examined. The sputtering conditions investigated are summarized in Table 1.

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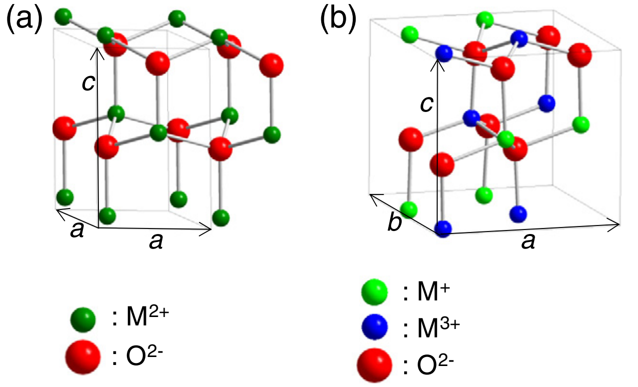

Fig. 1. Schematic illustrations of (a) hexagonal wurtzite and (b) orthorhombic β-$NaFeO_2$ crystal structures.

The phase in the obtained films was identified by θ-2θ X-ray diffraction (XRD; Rigaku, RINT2500, Cu Kα radiation). The chemical compositions of the films were determined by energy-dispersive X-ray (EDX) spectroscopy (EDAX, CDU-S; attached to a scanning electron microscope (SEM), JEOL, JSM-5600). The surface morphology of the films was observed with a SEM (JEOL, JSM-5600). Optical transmission spectra in the UV–Vis-NIR region were obtained using a Hitachi U4100 double-beam spectrometer in the wavelength range of 180–3300 nm. The photocurrent spectrum was measured by a two-probe method using a Model 487 picoammeter (Keithley Instruments Inc.) and a TR6143 voltage source (Advantest Co., Ltd.). Two gold electrodes, 200 nm thick, 2 mm wide with 0.5 mm spacing were sputtered onto the film. A 50 V dc potential was applied across the electrodes, and the current that flowed through the sample under irradiation by a monochromated xenon discharge lamp (SM-30, Bunkokeiki Co., Ltd.) was recorded as the photocurrent.

3. Results and discussion

XRD profiles of the films deposited under various sputtering gas atmospheres are presented in Fig. 2. Substrates were not intentionally heated, and the sputtering gas pressure was fixed at 0.25 Pa in these cases. The intense diffraction at $2\theta = 42°$ marked by an asterisk in the figure came from the Al_2O_3 substrate. For sputtering under a pure Ar gas atmosphere (Fig. 2(a)), a diffraction from metallic silver appeared, and no deposition of β-$AgGaO_2$ was observed.

For sputtering under a 10% O_2 atmosphere (Fig. 2(b)), only the (002) diffraction of β-$AgGaO_2$ was observed, indicating that the film consisted of (001)-oriented β-$AgGaO_2$ phase. It is well known that wurtzite-type phases, such as ZnO, usually form (001)-oriented films on a (0001)–Al_2O_3 substrate [20–22] despite the large lattice mismatch (18%) between ZnO and (0001)–Al_2O_3 [23]. Therefore, β-$AgGaO_2$ with a wurtzite-derived β-$NaFeO_2$-type structure may also be expected to form (001)-oriented films on a (0001)–Al_2O_3 substrate based on the similarly large lattice mismatch of 23.7% between β-$AgGaO_2$ and (0001)–Al_2O_3. Under 50% O_2 and pure O_2 atmospheres, the (002) and (121) diffractions of the β-$AgGaO_2$ phase appeared, respectively. A small and broad diffraction peak at $2\theta \approx 37°$ that could not be attributed to β-$AgGaO_2$ phase also appeared. If this diffraction peak was an indication of segregation of metallic silver, optical transparency of the film should also decrease. However, we did not detect any decrease in optical transmission, and the diffraction peak is concluded to not arise from metallic silver.

Table 1
Sputtering conditions used to deposit β-$AgGaO_2$ thin films.

Substrate	(0001)–Al_2O_3 single crystal
Gas flow rate	8 sccm
RF power	50 W
Deposition time	5 h
Substrate temperature	without intentional heating, 200 and 300 °C
Sputtering atmosphere	Pure Ar, 10% O_2-90% Ar, 15% O_2-85% Ar, 20% O_2-80% Ar, 25% O_2-75% Ar, 50% O_2-50% Ar, pure O_2
Pressure	0.25, 0.5 Pa

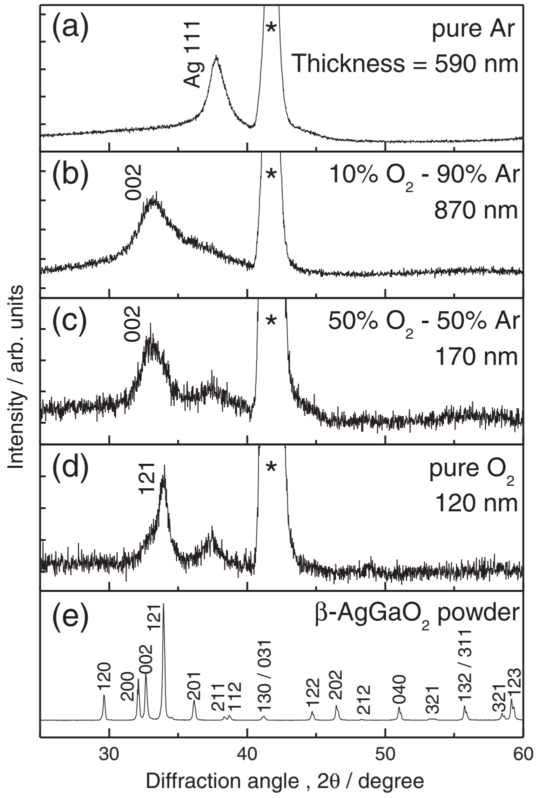

Fig. 2. XRD patterns of films deposited under various sputtering atmospheres at 0.25 Pa. Substrates were not intentionally heated during deposition. (a) Pure Ar, (b) 10% O_2, (c) 50% O_2, (d) pure O_2 and (e) β-$AgGaO_2$ powder. The peak marked by an asterisk is related to the substrate Al_2O_3.

From the viewpoint of deposition rate, deposition under a 10% O_2 atmosphere was the fastest among the three atmospheres tested resulting in deposition of the β-$AgGaO_2$ phase at 3.0 nm min^{-1}. This is because deposition rates generally decrease with increasing oxygen concentration of the sputtering atmosphere. Accordingly, the 10% O_2 atmosphere was the best sputtering atmosphere among those investigated because the deposited films, apparently consist of a single phase of β-$AgGaO_2$ and the deposition is comparatively fast.

The XRD peaks of the films deposited without intentional substrate heating are extremely broad (see Fig. 2(b)). This is attributed to the low crystallinity of these films. Therefore, we next attempted deposition with substrate heating to improve the crystallinity of the resulting films. Generally, oxide films are deposited at substrate temperatures higher than several hundred degrees centigrade to obtain highly crystallized films. However, β-$AgGaO_2$ decomposed into metallic silver and Ga_2O_3 when it was heated at temperatures higher than 600 °C in air. Therefore, we examined film deposition at 200 and 300 °C to suppress the decomposition of the β-$AgGaO_2$ phase. Fig. 3 shows the XRD patterns of the films deposited at 200 °C with various sputtering atmospheres at a pressure of 0.25 Pa. For deposition at 200 °C, metallic silver appeared even under a 10% O_2 atmosphere, as shown in Fig. 3(a). By increasing the O_2 concentration above 15% (Fig. 3(b)–(d)), the formation of metallic silver was suppressed, and (001)-oriented β-$AgGaO_2$ films were obtained. The observed (002) diffraction peaks were much sharper than those of the films deposited without intentional substrate heating. As expected, the crystallinity of the β-$AgGaO_2$ phase was improved by substrate heating.