



Compositional ratio effect on the surface characteristics of CuZn thin films

Ahrom Choi, Juyun Park, Yujin Kang, Seokhee Lee, Yong-Cheol Kang^{*}

Department of Chemistry, Pukyong National University, 45, Yongso-ro, Nam-Gu, Busan, 48513, South Korea



ARTICLE INFO

Keywords:

Copper
Zinc
Thin film
XPS
UPS
XRD

ABSTRACT

CuZn thin films were fabricated by RF co-sputtering method on p-type Si(100) wafer with various RF powers applied on metallic Cu and Zn targets. This paper aimed to determine the morphological, chemical, and electrical properties of the deposited CuZn thin films by utilizing a surface profiler, atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), UV photoelectron spectroscopy (UPS), and a 4-point probe. The thickness of the thin films was fixed at 200 ± 8 nm and the roughness of the thin films containing Cu was smaller than pure Zn thin films. XRD studies confirmed that the preferred phase changed, and this tendency is dependent on the ratio of Cu to Zn. AES spectra indicate that the obtained thin films consisted of Cu and Zn. The high resolution XPS spectra indicate that as the content of Cu increased, the intensities of Zn^{2+} decreased. The work function of CuZn thin films increased from 4.87 to 5.36 eV. The conductivity of CuZn alloy thin films was higher than pure metallic thin films.

1. Introduction

Cu is known to have excellent electrical conductivity, physical strength, and biochemical properties such as antibacterial activity [1]. Cu tends to exist as two oxidized compounds: Cu_2O and CuO . Cu_2O (cuprous oxide) is used as a semiconductor because of their band gap energy (~ 2.1 eV) [2], which led the material to being extensively studied for photovoltaic applications such as photocatalysis and solar cells [3,4]. In the case of CuO (cupric oxide), it also exhibits semiconducting properties with a band gap of 1.4 eV [2] and is frequently used for various gas sensing applications [5,6]. Cu is widely used as an alloying element; for instance, it is used to create bronze with Sn or brass with Zn. In case of Zn, steel objects such as Fe, Ni, or Al are plated with Zn as a means to prevent corrosion [7–9]. Moreover, zinc oxide (ZnO), an oxidation form of Zn, is applied in a variety of fields such as thin film transistors for solar cells [10,11] because of its wide direct band gap energy (~ 3.3 eV) [12] and large exciton binding energy (60 meV) [13]. In addition, ZnO nano-structured films are used for gas sensors [14,15], and biosensors [16].

The Cu-doped Zn system was investigated because the physical and chemical properties of Cu is similar to those of Zn. Many researches for Cu-doped ZnO thin films have been reported about enhancement of the conductivity [17], gas sensing ability [18,19], and photoluminescent properties [20,21]. K. G. Girija et al. and A. Sreedhar et al. reported highly selective gas sensors based on Cu-doped ZnO thin films by doping

Cu [18] and enhanced photoluminescence of violet emission with contents of Cu [20], respectively. Brass, which is the Cu and Zn alloy system, is applied in various fields such as wind instruments and biomedical materials [22,23] because of their beautiful color, antibacterial properties, relatively superb mechanical and physical properties [24]. J. Niu et al. reported mechanical and antibacterial properties of Zn-4 wt.% Cu alloy for potential vascular stents application [22]. Moreover, S. Hosseinpour et al. studied corrosion resistivity of Cu-Zn alloy [24]. Commonly used brass is α -brass which pertains to a Cu to Zn ratio of 60 to 40 and its properties have been studied [22–24]. However, there is a lack of research on the characteristics of Cu to Zn ratio.

There are various methods to fabricate thin films such as sol-gel techniques [25,26], chemical vapor deposition (CVD) [1,15], thermal evaporation [27], electrodeposition [28], and radio frequency (RF) magnetron sputtering [10,18,20,29]. Among these methods, the RF magnetron sputtering method is typically used to synthesize uniform thin films. [30] The chemical and physical properties of thin films were affected by a variety of parameters such as the RF power on the target, the type of sputter gas used, the working pressure, and the substrate temperature.

In this research, we fabricated CuZn thin films by controlling the Zn contents utilizing the RF magnetron co-sputtering method with various RF power on metallic targets at room temperature. The structural properties of the obtained CuZn thin films were investigated by a surface profiler, atomic force microscopy (AFM), and X-ray diffraction (XRD).

^{*} Corresponding author.

E-mail address: yckang@pknu.ac.kr (Y.-C. Kang).

The chemical and optical properties of the films were studied with electron emission spectroscopy such as, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and ultra-violet photoelectron spectroscopy (UPS). The electronic states of the valence level of the films were monitored by the Kelvin probe (KP) method. The electrical properties of the films were measured by a 4-point probe to exclude the effect of contact resistance.

2. Material and methods

CuZn thin films were deposited on p-type silicon (100) substrate by RF co-sputtering using metallic Cu (99.99%, VBM, Korea) and Zn (99.99%, VBM, Korea) targets with high purity Ar (99.99%) gas used as a sputter gas. The Si substrate was cleaned with acetone before it was placed on the substrate holder which was in the co-sputtering chamber. The flow rate of Ar gas was fixed at 20 sccm controlled by a mass flow controller. The base pressure of the co-sputtering chamber was maintained below 1.70×10^{-6} Pa and the working pressure was kept at 1.4 Pa by a turbo molecular pump (TMP) and a rotary vane pump (RP). The applied RF power on the targets was varied from 21 to 0 W for the Zn target and from 0 to 50 W for the Cu target. Before fabricating the CuZn thin films, it was necessary to determine the deposition rates of Cu and Zn targets for a constant thickness of the films. The thickness of pure Cu and Zn films was measured with a surface profiler (Alpha-Step 500, Tencor, USA). In order to determine the thickness of the films, the edge of the Si substrate was masked with thermal resistant tape before the sputtering process. Also, using the determined deposition rates of Cu and Zn films, the thickness of CuZn thin films was controlled at about 200 nm by varying the sputtering time. The notation of CuZn thin films used in this report is CuZnX and the X refers to the RF power applied on the Zn target. For example, CuZn21 denotes that the RF power on the Zn target was 21 W for this respective CuZn thin film. In order to remove the contaminants on the metallic targets and to stabilize the plasma, a pre-sputtering process was performed before the co-sputtering process for 10 min with the shields of the targets closed.

The roughness of the films was determined by AFM (Dimension FastScan, Bruker, USA) in tapping mode and estimated by root mean square (RMS) values. The scan size and the scan rate was $2.0 \times 2.0 \mu\text{m}^2$ and 0.7 Hz, respectively. The phase and crystallinity of the obtained films were studied with XRD (Ultima IV, Rigaku, Japan) which was operated with 40.0 kV of acceleration voltage, 40.0 mA of filament current, and 0.02° of scan step using Cu K α source in theta-2theta mode.

The chemical environment of the CuZn thin films was studied by XPS (ESCALab MKII, VG, UK) with Mg K α X-ray source (1253.6 eV) and AES. XPS was performed with a high voltage of 14 kV and a current of 20 mA for Mg K α X-ray source. AES was studied with an acceleration voltage of 3.0 kV, a filament current of 2.1 A, and a beam current of 0.5 mA. The base pressure of the analysis chamber was maintained below 4.1×10^{-7} Pa with RPs, TMPs, ion getter pumps, and a Ti-sublimation pump. The high resolution XPS spectra were collected with a concentric hemispherical analyzer (CHA) in constant analyzer energy (CAE) mode with a pass energy of 50 eV, a dwell time of 100 ms, and an energy step size of 0.05 eV with nine scans. The obtained XPS spectra was deconvoluted with the XPSPEAK software (version 4.1) in a Gaussian/Lorentz ratio (30/70) to determine the chemical environment of Cu, Zn and O. The AES spectra were collected with a CHA in constant retard ratio (CRR) mode with a kinetic energy to pass energy ratio of 4, a dwell time of 100 ms, and an energy step size of 0.5 eV with four scans at wide range, and an energy step size of 0.1 eV with nine scans at narrow range.

The work function of the films was determined by UPS (ESCALab MKII, VG, UK) with He I (21.2 eV) UV source at a bias of -10 V. UPS was studied with a current of 52 mA and a voltage of 0.61 eV at a pressure of 2.9×10^{-5} Pa. Also, the electronic states of the valence level of the films were determined by using a Kelvin probe (KP, KP6500, McAllister Technical Services, US). The work function of the probe was corrected by using Au and Pt metals as references prior to the calculation of work

functions of the CuZn films with KP. The electrical property of the films was determined by a 4-point probe (MCP-T6000, Loresta, Netherlands).

3. Results and discussion

The thickness of the obtained CuZn thin films was measured by a surface profiler. The thickness of the CuZn thin films was controlled at 200 ± 8 nm by adjusting the sputtering time. The deposition rates of Cu and Zn were obtained from the thickness, sputtering time, and atomic ratio as shown in Fig. 1. The atomic ratio of Cu and Zn were calculated from the high resolution XPS spectra of Cu 2p $_{3/2}$ and Zn 2p $_{3/2}$ considering the relative sensitivity factor of Cu and Zn. The deposition rates of Cu and Zn show a complementary propensity. As the RF power on Zn target increased, the deposition rate of Zn increased, while Cu decreased. The deposition rate of the pure Zn thin film was 42.7 nm/min when the applied RF power on Zn target was 21 W, and pure Cu thin film was 25.0 nm/min when the applied RF power on Cu target was 50 W. Although the applied RF power on the Zn target was lower than the Cu target, the deposition rate of pure Zn thin film was faster than pure Cu thin film.

The morphology and roughness of the CuZn thin films were investigated by AFM. Fig. 2(a)–(c) show the three-dimensional surface morphology images of CuZn0, CuZn9, and CuZn21 thin films, respectively. As the RF power on Zn target increased, the obtained thin films exhibited a rougher surface. The RMS roughness values (R_{rms}) of the thin films are 1.70 (CuZn0, pure Cu), 2.18 (CuZn9), and 25.3 nm (CuZn21, pure Zn). These results are consistent with previous works of M. T. Le et al. and B. R. Kumar et al. groups; the roughness of Zn thin films was larger than Cu thin films [31,32]. The average grain sizes of the thin films are 46.7 ± 2.0 (CuZn0), 56.6 ± 3.1 (CuZn9), and 667.7 ± 87.2 nm (CuZn21). The grain size increased as the RF power applied on Zn target increased. It indicates that the grain size was mainly governed by the contents of Zn in the film. The grains of Zn-rich thin film formed an island-like shape as shown in Fig. 2(c), while the grains of Cu-rich thin films comparatively formed needle-like or column-like morphology as shown in Fig. 2(a) and (b). The packing density of the columnar grains in pure Cu thin films (CuZn0) was larger than those of alloy thin films (CuZn9) because the grain size of CuZn0 films was smaller than CuZn9 films.

The phase and crystallinity of the obtained CuZn thin films were investigation by XRD and the diffractograms are shown in Fig. 3(a). The (200) phase of Cu (JCPDS no. 85–1326) was monitored from CuZn0 to CuZn6 thin films. The cubic Cu(111) (JCPDS no. 85–1326) phase at a peak position of 43.3° was detected from CuZn0 to CuZn13 and the peak

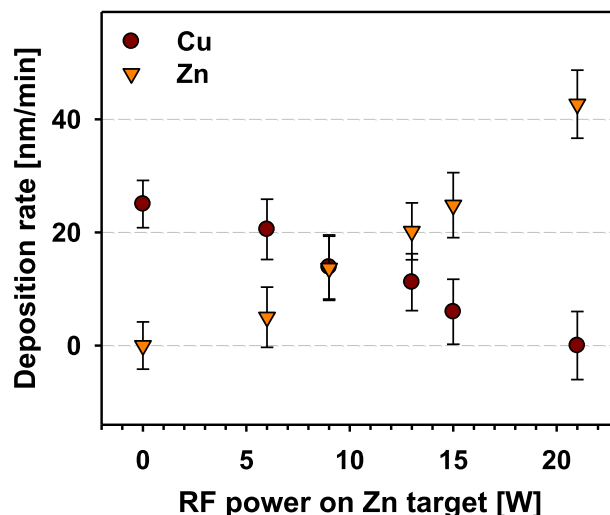


Fig. 1. Deposition rates of Cu and Zn of CuZn thin films.

Download English Version:

<https://daneshyari.com/en/article/8160904>

Download Persian Version:

<https://daneshyari.com/article/8160904>

[Daneshyari.com](https://daneshyari.com)