Optical and Structural Properties of a ZnS Buffer Layer Fabricated with Deposition Temperature of RF Magnetron Sputtering System

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Abstract—Optical properties of sputter-deposited ZnS thin films were investigated as potential replacements for CBD(chemical bath deposition) CdS buffer layers in the application of CIGS solar cells. ZnS thin films were fabricated on glass substrates at RT, 150°C, 200°C, and 250°C with 50 sccm Ar gas using an RF magnetron sputtering system. The crystal structure of the thin film is found to be zinc blende (cubic) structure. Lattice parameter of ZnS is slightly larger than CdS on the plane and thus better matched with that of CIGS. Within a 400-800 nm wavelength region, the average transmittance was larger than 75%. When the deposition temperature of the thin film was increased, the blue shift phenomenon was enhanced. Band gap energy of the ZnS thin film tended to increase as the deposition temperature increased. ZnS thin film is a promising material system for the CIGS buffer layer, in terms of ease of processing, low cost, environmental friendliness, higher transparency, and electrical properties

Keywords— ZnS thin film, Buffer layer, CIGS, Solar cell.

I. INTRODUCTION

THIN film solar cells have attracted research attention because of their high efficiency and low cost [1-2]. A CdS fabricated by chemical bath deposition (CBD) method has been widely used as a buffer layer for CIGS solar cell [1]. The CdS buffer layer has many advantages, including simple processing, low cost, and high efficiency of resulting solar cells [3].

The CdS, may cause serious environmental issues due to the Cd element [3]. Because the band gap of the CdS is 2.42 eV[4], transmittance rapidly decreases, and the efficiency of the solar cell also decreases at a shorter wavelength region. To overcome the current issue in the CdS layer, a new buffer layer, of larger band gap [1, 5], and environmentally-friendly manufacturing process, is required. Among many possible candidates, ZnS is the most promising material for this purpose [1, 6]. Because a

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Y. T. Oh is with the Department of Advanced Materials Engineering, Chosun University,375 Seosuk-dong, Dong-gu, Gwangju, 501-759, Korea (e-mail: yto02@chosun.ac.kr). band gap of ZnS equals 3.65 eV [3, 7], ZnS is perfectly transparent in visible light [1]. ZnS is also less toxic than CdS materials [4, 7].

The ZnS layer can be fabricated through several methods [3-4, 7]. Among varied methods, we used the sputtering method for the deposition of the ZnS buffer layer. ZnS thin films were deposited under varied experimental conditions. The microstructure and optical properties of the thin film were investigated.

II. EXPERIMENTAL CONDITIONS

A RF magnetron sputtering system was used to deposit the ZnS thin film, and glass was used as substrate and was cleaned using acetone, ethanol, and deionized (D.I) water before deposition. The Base pressure was less than 2.0×10^{-6} Torr. All the thin films were deposited at room temperature, with 50 sccm Ar gas flow. The RF powers were varied between 30, 50, 75, and 100 W, while deposition time was varied between 5, 10, 20, and 40 min.

The crystal structure of the deposited thin films was examined by X-ray diffraction (XRD, X'pert pro MPD, PANalytical). The thickness and surface of the microstructure were analyzed by scanning electron microscopy (FE-SEM, S-4800, Hitachi). Transmittance was measured by UV/VIS spectrometer (Lambda35, PerkinElmer).

III. RESULT AND DISCUSSION

Fig. 1 shows the thickness variation of the deposited ZnS thin films, according to the RF power and deposition time. As shown in Fig. 1, the thickness of the thin film was 4.46 nm at 5 min, with 30 W RF power, and increased to 16.2 nm at 40 min. Thickness varied from 9.81 nm to 56.1 nm at 50 W, from 17.2 to 111 nm at 75 W, and from 20.6 to 162 nm at 100 W. For the application of ZnS thin film to a CIGS buffer layer, we have to precisely control the thickness of the thin film. The thickness of the thin film is gradually increased, according to experimental conditions, which enables us to precisely control the thickness.

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Deposition time (min)

Fig. 1 Thickness variations of ZnS thin film according to RF power and deposition time. RF powers vary as 30, 50, 75, and 100 W. Deposition times vary as 5, 10, 20, and 40 min

The lattice parameter of a zinc blende structure is 5.4 Å, while that of wurtzite (hexagonal) CdS is 3.8 Å. The equivalent lattice parameter of cubic-like CdS is 5.38 Å. The lattice parameter of CIGS chalcopyrite phase is 5.8 Å. Fig. 2 shows a lattice mismatch between ZnS(111), CdS(0001), and CIGS(112) planes on the same plane. It is well known that the texturing plane of the CIGS is (112) plane. As shown in Fig. 2, the lattice parameter of ZnS is slightly larger than CdS on the plane and thus better matched with the that of CIGS.



Fig. 3 shows the transmittance of the thin film shown in Fig. 2. The numerical average transmittances between 400-800 nm were: 90.7 % at 30 W, 82.6 % at 50 W, 82.6 % at 75 W, and 69.0 % at 100 W. When the thickness increased, the transmittance showed a red shift.

Band gaps of material can be calculated through the absorption coefficient α as shown in Eq.(1):

$$(\alpha h v) = A(h v - E v)^{1/2}$$
(1)

where, A is constant, and hv is photon energy. The absorption coefficient, α , can be calculated through Eq.(2).

$$T = \exp(-\alpha d) \tag{2}$$

where T is transmittance of material and d is the thickness plotting $(\alpha hv)^2 vs (hv)$, we can calculate Eq value.



Fig. 3 Relative transmittance of ZnS thin film deposited at 30, 50, 75, and 100 W for 20 min

Fig. 4 shows the energy band gaps of all specimens in this study, according to thickness. The energy band gaps calculated from transmittance curves within 300 and 600 nm vary from 3.95 eV of a 4.46 nm thick thin film to 3.71 eV of a 162 nm thick thin film. Regarding deposition conditions, the band gap is gradually decreased according to the thickness of the thin film. The graph shows the red shift phenomenon and Eg converges to the bulk Eg value of ZnS. The higher Eg value ensures transmittance at wider wavelength regions, particularly short ones. The value of 3.83 eV is much higher than 2.4 eV of CdS buffer layer, which is favored-in terms of transmittance and electric property-in view of the intrinsic characteristics of the buffer layer of a CIGS solar cell.

Fig. 2 Lattice parameter comparison between (111) plane of zinc blende structure of ZnS, (0001) plane of wurtzite structure of CdS, and (112) plane of chalcopyrite structure of CIGS



Fig. 4 Variations of energy band gap according to the thickness of ZnS thin film. The dotted line indicates energy band gap of bulk ZnS

IV. SUMMARY

This study reveals ZnS thin film to be a promising candidate for the buffer layer of CIGS solar cells. The deposition rates of sputter-deposited ZnS thin films were not so quick that the thickness of the thin film could be precisely controlled by RF power and deposition time. The ZnS thin film, deposited at room temperature, showed zinc blende (cubic) structure with a lattice parameter of 5.4 Å. This lattice parameter is better matched with that of a CIGS chalcopyrite structure than with a CdS. Within a 400-800 nm wavelength region, the average transmittance was larger than 69 %. When the thickness of the thin film was increased, transmittance decreased, and the red shift phenomenon appeared. Compared to 3.6 eV band gap of bulk ZnS materials, all values of thin films have higher Eg value. Higher Eg value of ZnS thin film, compared to the CdS buffer layer, is beneficial to transparency and thus to the power efficiency of the CIGS solar cell. ZnS thin film is a promising material system for the CIGS buffer layer, in terms of ease of processing, low cost, environmental friendliness, higher transparency, and electrical properties.

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