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Pulsed laser deposition and characterization of epitaxial CuInS$_2$ thin films on $c$-plane sapphire substrates

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ABSTRACT

The epitaxial growth of CuInS$_2$ thin films on single-crystal sapphire (0001) substrates was first attempted by using pulsed laser deposition. A highly dense CuInS$_2$ ceramic target with chalcopyrite structure was prepared by sintering high-purity (5N) powders in vacuum at 960°C for an hour. CuInS$_2$ thin films deposited at various temperatures all grew in a (112) preferred orientation, suggesting a three-dimensional island-like growth mechanism. When deposited at 700°C, epitaxial growth of CuInS$_2$ films on $c$-plane sapphire was achieved with an out-of-plane orientation of CuInS$_2$ (112)$\parallel$sapphire (0001) and in-plane orientation of CuInS$_2$ [1\bar{1}0]$$\parallel$sapphire (10\bar{1}0). A typical rocking curve half width of 0.17° demonstrates a high degree of crystallinity as well as excellent alignment of the CuInS$_2$ films along [221], whereas in-plane two domains rotated by 180° with respect to each other are found coexisting in the epilayers. High-quality epitaxial thin films will allow further research into the fundamental properties of CuInS$_2$ absorber layers, which will eventually help to improve conversion efficiencies of CuInS$_2$-based solar cells.

Keywords: CuInS$_2$; epitaxial growth; thin film; pulsed laser deposition

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1. Introduction

In recent years, ternary I–III–VI$_2$ semiconductor compounds gained increasing interest for photovoltaic applications [1]. A promising material is the chalcopyrite compound CuInS$_2$ (CIS). It has a direct bandgap of $\sim$1.53 eV, well matching to the solar spectrum, with a high optical absorption coefficient of $10^5$ cm$^{-1}$. It can efficiently absorb sunlight in thin films thus minimizing the use of raw material, and it is less toxic compared to related compounds containing selenium. Moreover, it has theoretically the highest photoelectric conversion efficiency among the chalcopyrite Cu-III-VI$_2$ solar cells [2]. Although the development of photovoltaic devices has already reached the submodule level, the knowledge about fundamental properties of the CuInS$_2$ absorber layers is still limited [3]. Therefore, high-quality films such as epitaxial layers of CuInS$_2$ are called for.

So far, several methods have been used to deposit CuInS$_2$ thin films, such as single source evaporation [4], coevaporation of elemental sources [5], sulfurization of metallic precursors [6], chemical vapor deposition [7], sputtering [8], electrodeposition [9], atomic layer deposition (ALD) [10], spray pyrolysis [11], molecular beam epitaxy (MBE) [12, 13], and so on. Compared to these methods, pulsed laser deposition (PLD) offers obvious advantages in the preparation of high-quality CuInS$_2$ thin films. It enables a simple and flexible control of the film composition due to the high stoichiometric transfer from the target to the substrate. High degree of crystallinity can be obtained due to the enhanced surface migration of the pulsed laser induced highly energetic atoms [14]. By using a powder target, Kuranouchi et. al. had prepared CuInSe$_2$ thin films by pulsed laser deposition (PLD) and studied the annealing effects on the films [15]. In this study, we have first fabricated CuInS$_2$ ceramic target by sintering high-purity powders in vacuum, and then attempted to grow CuInS$_2$ thin films immediately by PLD on single-crystal $c$-plane sapphire.

As we previously reported [8], similar in-plane hexagonal symmetry, well-matched
lattice spacing, as well as comparable thermal expansion coefficients of CuInS$_2$ (112) and sapphire (0001) would allow a heteroepitaxial growth of CuInS$_2$ on $c$-plane sapphire. Although the side length of the sapphire (0001) plane (0.47587 nm) vs that of the CuInS$_2$ (112) plane (0.39222 nm) corresponds to a mismatch of approximately 17.6 %, the mismatch reduces to 1.1% when considering a group of five sapphire and six CuInS$_2$ hexagons. Therefore, magic epitaxy via domain matching is conceivable to occur in this system. Via optimization of the PLD process in terms of the substrate temperature, epitaxial growth of high-quality CuInS$_2$ thin films has been achieved on single-crystal sapphire (0001) substrates. Morphological, structural and compositional characterizations of the epitaxial films are reported in this paper.

2. Experimental

The CuInS$_2$ ceramic target was prepared by sintering high-purity (5N) powders in high vacuum (base pressure, $10^{-3}$ Pa) in a tube furnace (GSL 1600, KJMT, China). The powders were pressed to form a pellet, which was subsequently sintered at 960°C for 1 h and cooled in vacuum down to room temperature. In order to compensate the evaporation loss of Indium and Sulfur, some CuInS$_2$ powders were put around the pellet before sintering.

Prior to the deposition of CuInS$_2$ thin films, the $c$-plane sapphire substrates were marinated in H$_2$SO$_4$ : H$_2$O$_2$ = 1:1 solution for 10 min to remove part of the contaminations, then cleaned ultrasonically in organic solvents (acetone and ethanol) and rinsed in deionized water for 15 min sequentially. The vacuum chamber was evacuated to a base pressure of $10^{-4}$ Pa. The PLD was carried out using a KrF excimer laser (Lambda Physik COMPEX PRO 205 F, $\lambda = 248$ nm) set, with 150 mJ pulse energy and 5 Hz repetition frequency. All films were deposited during 30 min at various substrate temperatures of 100 °C, 300 °C, 500 °C and 700 °C, with thicknesses around 350 nm, 280 nm, 200 nm, and 125 nm, respectively, while
keeping the other parameters constant, in order to investigate the influence of substrate temperature on the film properties.

The crystal structures of the ceramic and thin films were studied by X-ray diffraction (XRD) using a four-circle diffractometer (Bruker, D8 discover) with Cu Kα (λ = 1.5418 Å) radiation. The cross-section morphology of the ceramic was observed by scanning electron microscopy (SEM; JSM 6700F), and the surface morphology of the films was characterized by using atomic force microscopy (AFM; DI, Nanoscope IIIa). Composition analyses of the ceramic and films were accomplished by X-ray photoelectron spectroscopy (XPS, SPECS PHOIBOS 150) at photon energy of 1486.6 eV (Al Kα radiation).

3. Results and discussion

Fig. 1 shows the cross-section SEM image of the CuInS₂ ceramic. It consists of grains of about 10 µm in size, having a density of 95% of the theoretical value. Compared to the CuInS₂ polycrystals (90% of theoretical density) prepared in a microwave oven by M. Susaki, our CuInS₂ ceramic is more compact [16]. Some liquid phase eutectic melt as found in CuInSe₂ [17] may have been formed during the sintering process, which led to lowered sintering temperature and densification of the CuInS₂ ceramic.

Fig. 2 shows the XRD spectrum of the CuInS₂ ceramic, in comparison with the standard spectrum of CuInS₂ (JCPDS file: 270159). It can be seen that, a nearly pure-phase CuInS₂ ceramic of chalcopyrite structure was obtained. Hence, from both the microstructure and phase-structure points of view, the home-made ceramic provides a good target for the following PLD growth of CuInS₂ thin films.

The AFM images of CuInS₂ films deposited at 100 °C, 300 °C, 500 °C, and 700 °C are displayed in Fig. 3 (a)-(d), respectively. The film deposited at 100°C exhibits a relatively smooth surface with a root-mean-square (RMS) roughness of approximately 8.24 nm, and
some agglomerates appear on the surface, which may result from the low mobility of surface atoms at low temperature. With increasing the substrate temperature, the film grains grow bigger, similar to what Unold et al. [18] reported for magnetron sputtered CuInS$_2$ films; simultaneously, the film RMS roughness increases almost linearly as illustrated in Fig. 3 (e). All films display a granular surface structure, indicating a three-dimensional island-like growth mechanism of the PLD grown CuInS$_2$ films.

Fig. 4(a) shows the XRD $\theta$-2$\theta$ spectra of CuInS$_2$ thin films deposited at various substrate temperatures. For films grown at 500 °C and 700 °C, besides diffraction peaks of the sapphire substrate, two peaks corresponding to the tetragonal chalcopyrite CuInS$_2$ (112) and (224) planes are clearly resolved, indicating a preferred orientation of CuInS$_2$ (112) parallel to sapphire (0001). For films deposited at 100 °C and 300 °C, only a weak (112) peak appears due to the inferior crystallinity obtained at low temperature. As seen from the narrow scan shown in Fig 4 (b), with increasing the substrate temperature, the diffraction angle of the (112) plane increases, meaning a decrease of the CuInS$_2$ (112) inter-planar distance according to the Bragg’s law. Compared to the relaxed CuInS$_2$ powder, the diffraction angles of all deposited films are somewhat smaller, indicating occurrence of certain expansions of the (112) lattice spacing in the films. Therefore, the CuInS$_2$ films are under tensile stress along the growth direction, and the stress is gradually released with increasing substrate temperature. Moreover, the full width at half maximum (FWHM) of the 2$\theta$ peak, reflecting the grain size in the case of polycrystals and the diffraction coherent length in the case of epitaxial layers, decreases from 0.59° for 100 °C to 0.14° for 700 °C, implying a significant improvement of the crystallinity of the films with increasing the substrate temperature.

The out-of-plane ordering of the films was further evaluated by rocking curve measurements. Shown in Fig. 5(a) are the normalized rocking curves of the CuInS$_2$ (112) plane for films deposited at 300 °C, 500 °C and 700 °C. With increasing the substrate
temperature for deposition, the rocking curve becomes narrower, indicating an enhancement of the out-of-plane ordering of the films. A FWHM value of 0.17° reveals an excellent alignment of the film deposited at 700 °C along [221]. This value is fairly comparable to those reported for CuInS$_2$ films epitaxially grown on Si (111) by MBE [12, 13] and for films grown on sapphire (0001) by RF reactive sputtering [19].

To achieve information on the in-plane ordering as well as determine the epitaxial relationship between the films and the substrate, XRD Phi scans were further performed. Fig. 5(b) shows the Phi-scan spectrum recorded at CuInS$_2$ {204} (Chi = 35.85°, 20 = 46.3°) for the film deposited at 700 °C, along with that for sapphire {104} (Chi = 38.65°, 20 = 35.15°). Sharp distinct reflexes show up representing the well-defined azimuthal alignment of the CuInS$_2$ lattice planes. Hence, the excellent out-of-plane ordering combined with the good in-plane ordering of the CuInS$_2$ lattice planes, as revealed by the rocking-curve and Phi-scan measurements, respectively, manifests unambiguously an epitaxial growth nature of the CuInS$_2$ film on sapphire. Similar to CuInS$_2$ epilayers on Si (111), six peaks, instead of three peaks as expected for single-crystal CuInS$_2$, are observed due to the twinned structure of the CuInS$_2$ film with two domains that are rotated by 180° to each other coexisting in the film. From the Phi-scan measurements, an in-plane orientation relationship between the CuInS$_2$ epilayer and the sapphire substrate can be inferred, that is, CuInS$_2$ [110]∥sapphire (1010), according to what we previously found in the sputter grown epitaxial CuInS$_2$ films on c-plane sapphire [8].

Stoichiometry control of the ternary compound CuInS$_2$ is often non-trivial but has profound influence on its optical and electrical properties. Whereas the sintered CuInS$_2$ ceramic target is slightly S deficient, the films deviate largely from the nominal stoichiometry in terms of the S concentration, in particular, when deposited at a high substrate temperature. Fig. 6 presents the XPS spectra of a CuInS$_2$ film deposited at 700 °C. The spectra were all
obtained after Ar-etching for sufficient time to remove the surface contaminants. As seen in the survey spectrum shown in Fig. 6(a), signals from all elements Cu, In, and S are present as expected. In addition, trace signals of C and O are detectable, indicative of minute contamination of the film in the bulk. The main elements concentration was quantified based on the narrow-scan spectra of Cu 2p, In 3d, and S 2p (cf. Fig. 6b), resulting in Cu:In:S = 1.05:1:1.38. It is obvious that the PLD deposition of CuInS$_2$ at high temperature of 700 °C caused significant loss of S, due to the low melting point and thus high vapor pressure of sulfur. To maintain the desired stoichiometry of CuInS$_2$, either supply of S-containing gases like H$_2$S during the PLD process or post-growth sulfurization is thus necessary. Preliminary experiments have shown that annealing of the PLD grown CuInS$_2$ films at 300 °C in S vapor is efficient to achieve stoichiometric CuInS$_2$ films. Detailed characterization of the annealed/sulfurized CuInS$_2$ films is underway and the results will be published elsewhere [20].

4. Conclusions

Compact and nearly pure-phase chalcopyrite CuInS$_2$ ceramics have been sintered successfully in high vacuum. Using the self-made ceramic target, high-quality CuInS$_2$ thin films were deposited on c-plane sapphire substrates by PLD. All CuInS$_2$ films deposited at various temperatures grew in a (112) preferred orientation, and showed a three-dimensional island-like growth mode. Epitaxial growth was achieved at a substrate temperature of 700 °C, with an epitaxial relationship between the CuInS$_2$ layer and sapphire substrate of CuInS$_2$(112)||sapphire (0001) and CuInS$_2$ [ 1 1 0 ] ||sapphire (10 1 0) for the out-of-plane and in-plane orientations, respectively. A typical rocking curve half width of 0.17° demonstrates an excellent out-of-plane ordering of the films, whereas in-plane two domains rotated by 180° to each other are found coexisting in the epilayers. High-quality epitaxial thin films offer good
samples for further research into the fundamental properties of CuInS$_2$ absorber layers, which will eventually help to improve conversion efficiencies of CuInS$_2$-based solar cells.

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Figure captions:

Fig. 1. SEM image of the CuInS$_2$ ceramic sintered in high vacuum at 960 °C for 1h.

Fig. 2. (Color online) XRD spectrum of the CuInS$_2$ ceramic sintered in high vacuum at 960 °C for 1h.

Fig. 3. (Color online) AFM images of CuInS$_2$ thin films deposited on c-plane sapphire at (a) 100 °C, (b) 300 °C, (c) 500 °C, (d) 700 °C, respectively, and (e) the change of RMS roughness versus the substrate temperature during deposition.

Fig. 4. (Color online) (a) XRD $\theta$-2$\theta$ spectra of CuInS$_2$ thin films deposited at 100 °C, 300 °C, 500 °C, and 700 °C, respectively, (b) XRD narrow scan spectra of the films.

Fig. 5. (Color online) (a) XRD rocking curves for the (112) plane of CuInS$_2$ thin films deposited at 100 °C, 300 °C, 500 °C, and 700 °C, respectively, (b) In-plane Phi scan recorded at CuInS$_2$ {204} with a tilt angle (Chi = 35.85°, 2$\theta$ = 46.3°) of 35.5° for the film deposited at 700 °C, along with that for sapphire {104} (Chi = 38.65°, 2$\theta$ = 35.15°).

Fig. 6. (a) Survey-scan XPS spectrum and (b) narrow-scan XPS spectra of Cu 2p, In 3d, and S 2p of the CuInS$_2$ thin film deposited at 700 °C.
Figure 5

(a) Normalized intensity vs. Theta (degree) for 300°C, 500°C, and 700°C.

(b) Intensity (a.u.) vs. Phi (degree) showing peaks for Sapphire {104} and CIS {204}.
Highlights:

► A highly dense CuInS$_2$ ceramic target with chalcopyrite structure was sintered in high vacuum.

► Epitaxial growth of CuInS$_2$ thin films on sapphire (0001) substrates was achieved by PLD at 700 °C.

► Epitaxial relationship is CuInS$_2$ (112)$\parallel$ sapphire (0001) while CuInS$_2$ [1 1 0]$\parallel$ sapphire (10 1 0).

► A rocking curve half width of 0.17° demonstrates an excellent out-of-plane ordering of the films.

► In-plane two domains rotated by 180° to each other are found coexisting in the epilayers.