한국전기전자재료학회 2001년도 하계학술대회 논문집

$CuGaS_2$ 반도체 박막의 구조적 및 전기적 특성

Structural and Electrical Properties of $CuGaS_2$ Thin Films

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Abstract

Single phase $CuGaS_2$ thin film with the highest diffraction peak of (112) at diffraction angle (2θ) of 28.8 ° was made at substrate temperature of 70 ℃, annealing temperature of 350 ℃ and annealing time of 60 min. And second highest (204) peak was shown at diffraction angle (2θ) of 49.1 °. Lattice constant of a and c of that $CuGaS_2$ thin film was 5.37 Å and 10.54 Å respectively. The greatest grain size of the thin film was about 1 ㎛ . The (112) peak of single phase of $CuGaS_2$ *thin* film at annealing temperature of 350 ℃ with excess S supply was appeared with a little higher about 10 % than that of no exces S supply And the resistivity, mobility and hole density at room temperature of p-type $CuGaS_2$ thin film with best crystalline was 1.4 Ωcm, 15 cm2/V · sec and $2.9\times 10^{17}cm^{-3}$ respectively. It was known that carrier concentration had considerable effect than mobility on variety of resistivity of the fabricated $CuGaS_2$ thin film, and the polycrystalline $CuGaS_2$ thin films were made at these conditions were all p-type.

Key Words : Single phase, Lattice constant , Grain size, Resistivity, Mobility, Hole density

1. Introduction

The ternary chalcopyrite semiconductor copper gallium disulphide($CuGaS_2$) attracts much attention because it has a direct band gap and energy band gap of about 2.49 eV in the green at room temperature. It's expected to be a promising material for optoelectronic device applications such as green light emitting devices. Also, it's suggested to be a possible material for the window layer of Cu-Ⅲ-VI_2(Ⅲ=In,Ga and Ⅵ=S,Se) solar cell.

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However, the crystallinity and purity in this material are far behind compared with those in Ⅲ-Ⅴ or Ⅱ-Ⅵ compounds. Therefore, it is essential to establish the thin film technology of $CuGaS_2$ with high crystalline quality for advanced device. Also, the p-type $CuGaS_2$ is requested to have a sufficiently low resistivity for fabricating junction devices. Electron Beam Evaporation(EBE) techniques have never been examined in preparing $CuGaS_2$ thin films, as far as we know. And in the sulfurization of the S/Ga/Cu stacked layer, to compensate the compositional shift due to desorption of S during the annealing, excess S has to be supplied as the S layer several times thicker than required for the stoichiometric composition.

In this paper, we reported for the first time the successful growth of $CuGaS_2$ thin film by EBE methods. $CuGaS_2$ thin films were fabricated by annealing in vacuum the stacked layer (Cu/Ga/S/TCO) deposited by sequence on TCO glass substrate with various temperature and time. And optimum conditions for single phase $CuGaS_2$ formation, structural and electrical characteristics were investigated.

2. Experiment

Firstly, S/Ga/Cu stacked layers were prepared by sequential EBE of S, Ga and Cu with thickness of 11,000Å, 4,200Å and 2,500Å respectively for stoichiometric composition of $CuGaS_2$ on TCO glass substrate at 10^{-6} Torr. At this time, the sulfur was well deposited at the temperature of substrate of 70 ℃, and $CuGaS_2$ thin films were made by annealing temperature of 250℃~500℃ and annealing time 30 min ~120 min at vacuum 10^{-3} Torr of the stacked layers in order to determine the dependance of the room temperature resistivity and carrier density on the annealing conditions. Besides, in the sulfurization of the S/Ga/Cu stacked layer, to compensate the compositional shift due to desorption of S during the annealing, excess S has to be supplied as the S layer several times thicker than required for the stoichiometric composition. The thickness of $CuGaS_2$ thin film was about 1.7㎛ which was enough to obtain 1×10^{5} cm^{-1} of absorption coefficient. Secondly, structural and electrical characteristics were analyzed by X-ray diffractor (XRD), scanning electron microscope(SEM), 4-point probe method system and hall effect measurement apparatus over the temperature -250 ℃ ~ +250 ℃.

3. Results and Discussion

3.1 Structural properties

We found that annealing temperature had great effects on the growth of polycrystalline $CuGaS_2$ thin film rather than annealing time. X-ray diffraction patterns of as-grown $CuGaS_2$ thin films which were fabricated by various annealing temperatures were shown in Figure 1. The multiphases of $CuGaS_2$, Ga_2S_3 , GaS, Cu_2S, CuS and Ga were appeared until annealing temperature of 250 ℃ at all annealing times. The (112) peak of single phase $CuGaS_2$ thin film was showed at annealing temperature of 300 ℃ and annealing time 60 min. The highest (112) peak of single phase of $CuGaS_2$ was made by annealing temperature of 350 ℃, time of 60 min and substrate temperature of 70 ℃ appeared at diffraction angle (2θ) of 28.8 °. And second highest (204) peak was shown at diffraction angle (2θ) of 49.1 °. This XRD analysis confirmed that the formed material was $CuGaS_2$ with chalcopyrite structure. Annealing temperature of 350 ℃ and annealing time of 60 min was most appropriate for accepting single phase $CuGaS_2$ thin film with best crystalline. From extrapolation with Miller index, Bragg condition equation and Nelson-Riley correction equation, lattice constant of a and c of that $CuGaS_2$ thin film was accepted as 5.37 Å and 10.54 Å respectively . Photo. 1 showed SEM micrograph of the $CuGaS_2$ thin film. The greatest grain size of the thin film was about 1 ㎛ . The surface color of $CuGaS_2$ thin film was dark-green.

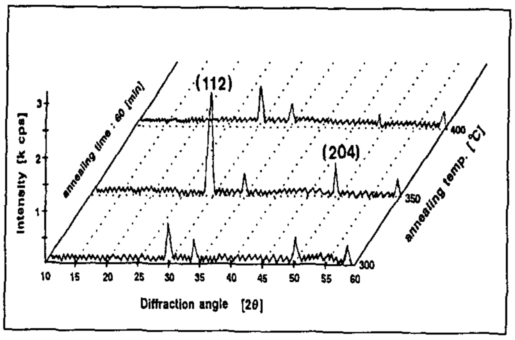

Fig. 1. XRD pattern of CuGaS2 thin films by annealing temperature.

But, over the annealing temperature of 400 ℃, the intensity of XRD became lower than 350 ℃.

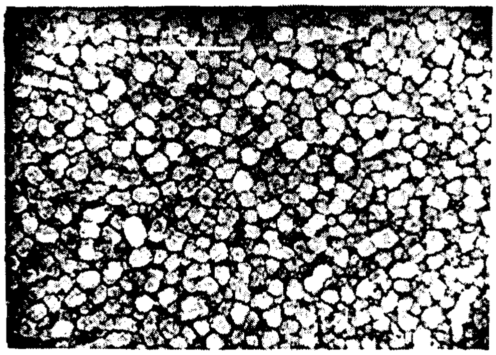

Photo. 1. SEM photograph of $CuGaS_2$ thin film at annealing temperature of 300 ℃.

In addition, annealing temperature of 500 ℃ occurred sometimes peeling at the surface of the thin film. At over 400℃, the higher annealing temperature was, the grain size was getting a little larger than that of 350 ℃. We think that it was over-annealed.

And the peaks of multiphases of $CuGaS_2$, Ga_2S_3, GaS, Cu_2S and CuS also appeared until 250 ℃ with excess S supply. The (112) peak of single phase of $CuGaS_2$ thin film at annealing temperature of 350 ℃ with excess S supply was appeared a little higher about 10 % than that of no exces S supply.

3.2 Electrical properties

Resistivities were measured to identify the conductivities of $CuGaS_2$ thin films. We found that the polycrystalline $CuGaS_2$ thin films were made at these studies were all p-type. At first, we measured the measurement temperature dependence of the resistivity at different annealing temperature. Figure 2 showed resistivies by annealing temperature. The room temperature resistivity of $CuGaS_2$ thin film varied from 94.8 Ωcm at annealing temperature of 250 ℃ to 0.75 Ωcm at annealing temperature of 500 ℃. And the resistivity of $CuGaS_2$ thin film with annealing temperature of 350 ℃ at room temperature was 1.4 Ωcm. It's value showed sufficiently high conductivity for fabricating junction devices.

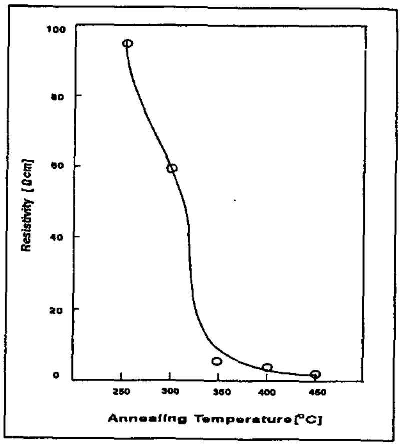

Fig. 2. Resistivities of $CuGaS_2$ thin films by annealing temperature.

Secondly, we measured the measurement temperature dependence of the carrier concentration at different annealing temperature. It showed well the hole concentration versus the reciprocal of temperature. Thirdly, we measured the measurement temperature dependence of the mobilities at different annealing temperature. It was seen quantitatively that the room temperature mobility is low, about 15 $cm^2/V \cdot sec$. As the temperature was lowered , the mobility was seen to increase until a property turning point was reached.

Figure 3 represented carrier concentrations and mobilities of $CuGaS_2$ thin films by annealing temperature. The room temperature hole density varied from $1.4 \times 10^{16} cm^{-3}$ to $1 \times 10^{18} cm^{-3}$. And the hole density of $CuGaS_2$ thin film with annealing temperature of 350 ℃ at room temperature was $2.9 \times 10^{17} cm^{-3}$. For the annealing temperature below 300 ℃, it was found that the hole concentration was several orders of magnitude lower. Besides, mobility was increasing until annealing temperature 350 ℃. The highest mobility was 15 $cm^2/V \cdot sec$ at 350 ℃. On the contrary, mobility decreased over annealing temperature 400 ℃.

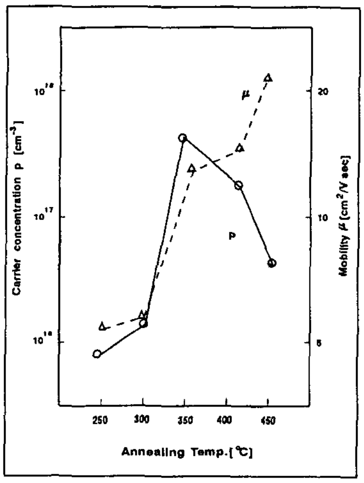

Fig. 3. Carrier concentrations and mobilities of $CuGaS_2$ thin films by annealing temperature.

Until annealing temperature 350 ℃, the variety of resistivity was well corresponded with the varities of carrier concentration and mobility. Namely, as the resistivity decreased, the carrier concentration and mobility increased together. But over the annealing temperature of 400 ℃, as the resistivity decreased, the carrier concentration also increased and on the contrary the mobility decreased. We knew that the larger grain size was, the crystalline defects increased and at last mobility decreased by decrease of energy barrier of carrier transfer. It seems clear that intrinsic defects are playing a major role in determining the conductivity, It is not certain whether annealing created shallow intrinsic acceptor (namely Cu vacancies or S interstitials) or removed intrinsic donors (namely Cu interstitials or S vacancies). We think that carrier concentration had considerable effect than mobility on variety of resistivity of the fabricated $CuGaS_2$ thin film.

4. Conclusion

$CuGaS_2$ thin film with the highest diffraction peak of (112) at diffraction angle (2θ) of 28.8 ° was well made at substrate temperature of 70 ℃, annealing temperature of 350 ℃ and annealing time of 60 min. Lattice constant of a and c of that $CuGaS_2$ thin film was accepted as 5.37 Å and 10.54 Å respectively . At over 400℃, the higher annealing temperature was, the grain size was getting a little larger than 1 μm of 350 ℃. And resistivity, mobility and hole density of $CuGaS_2$ thin film with annealing temperature of 350 ℃ at room temperature was 1.4 Ωcm, 15 $cm^2/V \cdot sec$ and $2.9\times10^{17}cm^{-3}$ respectively. But over the annealing temperature of 400 ℃, as the resistivity decreased, the carrier concentration also increased and on the contrary the mobility decreased. We found that $CuGaS_2$ thin films with low resistivity p-type can be made, but n-type conductivity appears difficult or impossible to achieve.

We concluded that the polycrystalline $CuGaS_2$ thin films were made at these conditions were all p-type and appropriate for wide band gap layer of Ⅰ-Ⅲ-$Ⅵ_2$.

References

[1] S.Shirakata, S.Chichibu, J.Appl.Phys.,879(8), 3793 (2000).

[2] T.Tinoco, J.P.Itie, A.Polian, A.San Miguel, E.Moya, P.Grima, J.Gonzalez, JOURNAL DE PHYSIQUE, 4, C9-151 (1994).

[3] T.Honda, H.Otoma, K.Hara, J. Yoshino and H. Kukimoto, J.J.Appl.Phys.,32(4B), L560(1993).1.

[4] M.Susaki, H.Horinaca and N. Yamamoto, J.J.Appl.Phys.,30(11A), 2797(1991).

[5] K.Hara, T.Shinozawa, J.Yoshino and H.Kuk-imoto, Journal of Crystal Growth 93, 771 (1988).

[6] H.Miyake, M.Hata and K. Sugiyama, Journal of Crystal Growth 130, 383 (1993).

[7] K. Oishi, S. Kobayashi, F. Kaneco, Journal of Crystal Growth 153, 158 (1995).

[8] J.J.M. Binsma, W.J.P. Enckevort and G.W.M. Staarink, Journal of Crystal Growth 61, 138 (1983).

[9] K.Hara, T. Kojima and H.Kukimoto, J.J.Appl.Phys.,26(7),L1107(1987).

[10] S.Wagner, J.L.Shay , B.Tell and H.M.Kasper, J.Appl.Phys.Lett., 22(8), 351(1973)