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TEM INVESTIGATION OF $CuInSe_2$-ZnSe HETEROSTRUCTURES FOR THIN FILM SOLAR CELLS

S.N. Grigorov, V.M. Kosevich, S.M. Kosmachev, A.V. Taran

National Technical University "Kharkov Politecnical Institute", 21, Frunze st., Kharkov, 61002, Ukraine; E-mail: ataran@kpi.kharkov.ua

In the article, $CuInSe_2$ thin films obtained by sequential deposition of Cu and indium selenide starting layer with the further annealing of the two-layered composition in Se atmosphere were investigated by transmission electron microscopy (TEM). On the base of the obtained basic $CuInSe_2$ layers, the ZnSe buffer layers were grown. It was found that ZnSe layer of cubic modification grow epitaxialy on a surface of $CuInSe_2$.

INTRODUCTION

$CuInSe_2$ (CIS) and ZnSe compounds are the promising candidates for basic and buffer layers for highly efficient thin film solar cells [1, 2]. The aim of the present contribution was to study a possibility of syntheses of large-crystalline $CuInSe_2$ thin films by activating solid-phase reactions in the two-layered In_2Se_3-Cu film composition with the following formation on their base $CuInSe_2$-ZnSe heterosystems.

The interest to zinc selenide films (ZnSe) is to find an alternative to cadmium sulfide (CdS) compound, which at present is usually utilized as a buffer layer in solar cells based on $CuInSe_2$(CIS) absorbers as well as in other chalcopyrite semiconductors of $A^1B^{111}X^{VI}$ type. Moreover, the motivation for searching an alternative to CdS buffer layer is in toxicity of cadmium containing material, which restrains its broad utilization. Besides that, ZnSe buffer layer is more advantageous in contrast with CdS one. For instance, forbidden gap (Eg = 2.67 eV) for ZnSe is wider in comparison with the (Eg = 2.42 eV) for CdS. This allows transmitting the high-energy photons from blue area of solar spectrum. Secondly, the crystalline lattice of ZnSe correlates well with crystalline lattice of absorber from $A^1B^{111}X^{VI}$, instead of CdS compound.

1. EXPERIMENTAL

In a present activity, the $CuInSe_2$-ZnSe thin films were deposited in a standard vacuum installation under $5 \cdot 10^{-3}$ Pa on glass-ceramic substrates.

The $CuInSe_2$ basic layers were prepared using sequential deposition of indium selenide and copper with the following annealing of the two-layered composition in a Se atmosphere (selenization) [3]. For the deposition of CIS, two schemes were applied (Fig.1,a,b). In one case, indium selenide was deposited using two-stage scheme: In_2Se_3 (substrate temperature T_{sub}=250 ºC) + Se (T_{sub}=350 ºC) + In_2Se_3 (T_{sub}=500 ºC) + Se (T_{sub} =550 ºC). In the other case, indium selenide was condensed in one turn at the temperature of 300ºC without additional selenization. For the preparation of indium selenide films a powder of In_2Se_3 at purity 99,999% and tablets of selenium (purity 99,9999%) were used. Indium selenide and selenium were evaporated from alundum crucibles.

To achieve effusion evaporation of selenium, a crucible with selenium tablets was closed with a tantalum cap with a small hole.

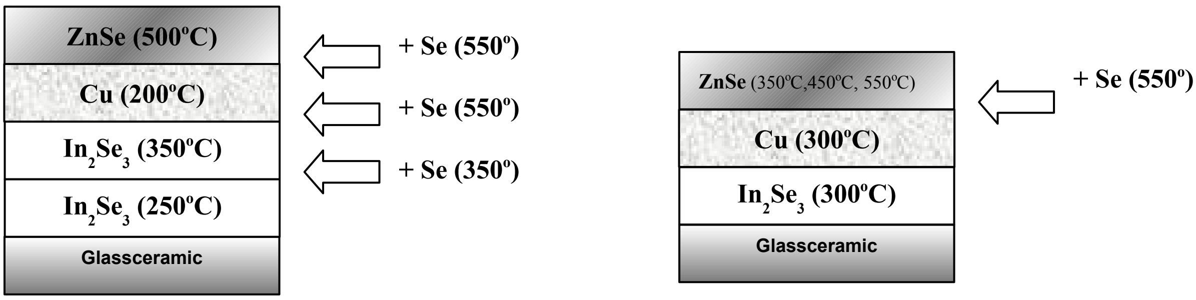
Copper (purity 99,999%) was deposited onto In(Se) layer at T_{sub} =200 ºC in the first case and at T_{sub}=300 ºC in the second case. Next, the two-layer In_2Se_3-Cu composition was selenized under T_{sub}=550 ºC. Zink selenide was evaporated from molybdenum boat and was deposited on surfaces of two-layered In_2Se_3-Cu film at T_{sub}=350, 450, 500 ºC and T_{sub}=550 ºC.

The structure and phase composition of the obtained samples were examined with the help of transmission electron microscopy.

2. RESULTS AND DISCUSSION

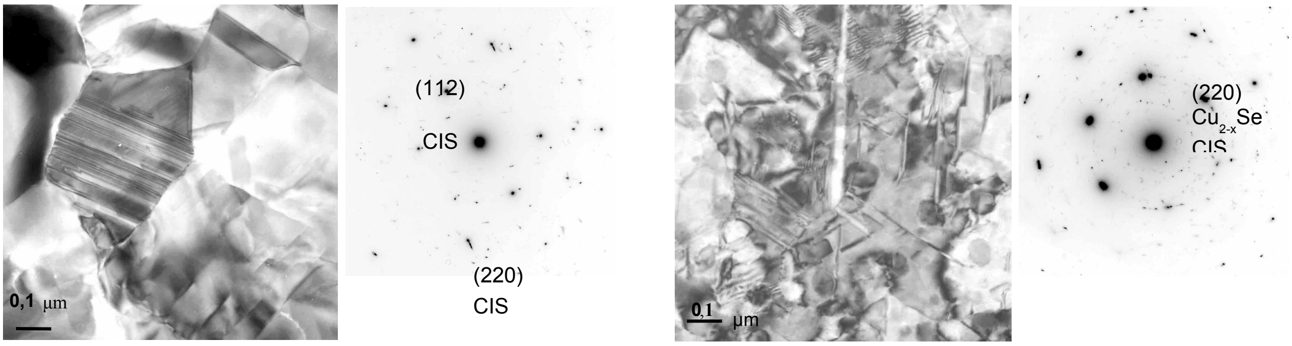
A typical structure and micro-diffraction pattern of the $CuInSe_2$ thin films deposited using two deposition sequences are presented in Fig.2. It was revealed that in both cases the large-crystalline grains of 1 µm in size were formed.

However, in CIS films, whereas the starting In_2Se_3 layer was deposited in two steps, the crystallites had more perfect structure (Fig.2,a), than in CIS films grown with a single In_2Se_3 layer (Fig.2,b). In CIS films of the second type the grains contained micro-twins. Besides that, we revealed some isles of the $Cu_{2-x}Se$ phase on the surface of these films. Obviously, the thickness of the Cu layer turned to be larger than it was required for the formation of CIS with stoichiometris composition.



a *b*

Fig.1. Crystal growth of $CuInSe_2$-ZnSe heterostructures



a *b*

Fig.2. TEM images and microdiffraction patterns of $CuInSe_2$ thin films, obtained using different deposition sequences

The Fig.3 presents an electron-microscopic image and microdiffraction pattern of the $CuInSe_2$-ZnSe heterostructure deposited by a method depicted in Fig.1,a. The moiré contrast was observed from (220) planes of CIS and ZnSe phases. This is an evidence of epitaxial grows of ZnSe on a surface of copper and indium deselenide film.

The moiré period of D_M=100 Å correlates well with the period (D_M = 102 Å), calculated for parallel orientation of (220) type planes of CIS and cubic ZnSe. The distortion of the moiré picture indicated the fact that zinc selenide film has a blocked structure with the blocks of ~0,1 μm in size. Such a structure is formed at growing ZnSe on island mechanizm.

The Fig.4 presents an electronic-microscopic images and microdiffraction patterns of $CuInSe_2$-ZnSe heterostructures produced on scheme Fig.1,b.

In all cases on a surface of CIS film, a polycrystalline ZnSe film of cubic modification was grown. The ZnSe thin film was formed due to existence of cooper selenide islands on a surface of CIS grains. The grain size in ZnSe films increases from ~20 nm with the temperature increase to T_{sub}=350 ºC and to about 100 nm at T_{sub}=550 ºC. Some ZnSe crystallites contained twinned lamellas.

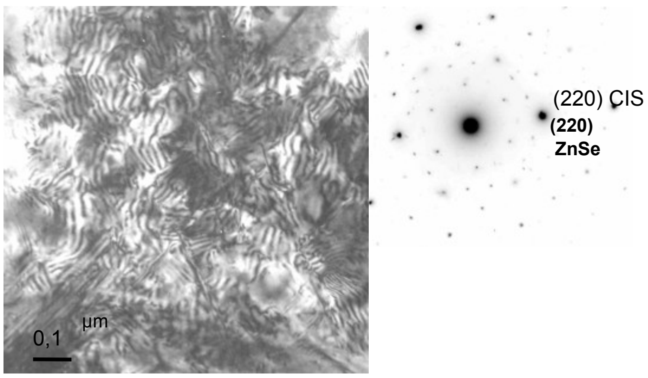


Fig.3. TEM image and microdiffraction pattern of the $CuInSe_2$-ZnSe heterostructure deposited by a method depicted in Fig.1a

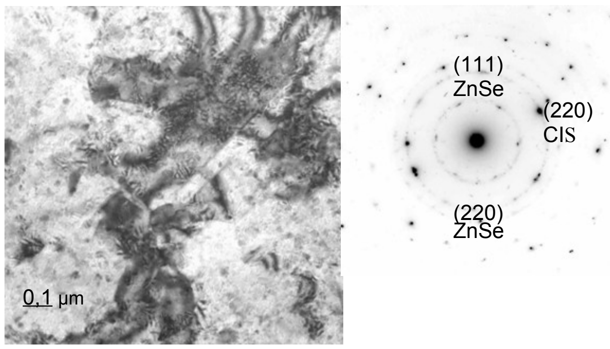


Fig.4. TEM image and microdiffraction patterns of CIS-ZnSe heterostructures produced on scheme Fig.1b

CONCLUSIONS

The phase composition and structure of $CuInSe_2$ and $CuInSe_2$-ZnSe films were investigated by transmission electron microscopy. It was revealed, that $CuInSe_2$ films formed on the base of two-layer composition of In_2Se_3-Cu were large-crystalline with the grain size of ~1 µm. The typical defects of the $CuInSe_2$ crystallites are microtwins. Zinc selenide of cubic modification grow on the surface of CIS films in epitaxial orientation at $T_{sub} = 500$ °C.

The ZnSe films are formed on island mechanism and have a block structure. The size of blocks was 0,1 µm. A polycrystalline zinc selenide film of cubic modification grow on a surface of $CuInSe_2$ thin films contained some isles of the $Cu_{2-x}Se$ phase under the substrate temperatures of T_{sub}=350, 450 and 550 °C. A principle possibility of formation of $CuInSe_2$-ZnSe heterostructure in one in-line vacuum process was shown.

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ЭЛЕКТРОННО-МИКРОСКОПИЧЕСКОЕ ИССЛЕДОВАНИЕ ГЕТЕРОСИСТЕМЫ $CuInSe_2$-ZnSe ДЛЯ ТОНКОПЛЁНОЧНЫХ СОЛНЕЧНЫХ ЭЛЕМЕНТОВ

С.Н. Григоров, В.М. Косевич, С.М. Космачев, А.В. Таран

Проведено электронно-микроскопическое исследование тонких плёнок $CuInSe_2$, приготовленных методом последовательного осаждения в вакууме селенида индия и меди с последующим отжигом двухслойной композиции в атмосфере селена. На основе полученных плёнок $CuInSe_2$ были выращены буферные слои ZnSe. Установлено, что слой ZnSe кубической модификации растёт эпитаксиально на поверхности плёнки $CuInSe_2$.

ЕЛЕКТРОННО-МІКРОСКОПІЧНЕ ДОСЛІДЖЕННЯ ГЕТЕРОСИСТЕМИ $CuInSe_2$-ZnSe ДЛЯ ТОНКОПЛІВКОВИХ СОНЯЧНИХ ЕЛЕМЕНТІВ

С.Н. Григоров, В.М. Косевич, С.М. Космачев, А.В. Таран

Проведено електронно-мікроскопічне дослідження тонких плівок $CuInSe_2$, виготовлених засобом послідовного осадження у вакуумі селеніду індію й міді з наступним відпалом двошарової композиції в атмосфері селену. На основі отриманих плівок $CuInSe_2$, були вирощені буферні шари ZnSe. Встановлено, що шар ZnSe кубічної модифікації зростає епітаксійно на поверхні плівки $CuInSe_2$.