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Impact of plasma nanostructuring on the electrical properties of Cu(In,Ga)Se$_2$ films

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Abstract. In this work, the impact of the plasma treatment, during the formation of nanostructure arrays on the surface of the Cu(In,Ga)Se$_2$ films on glass substrates, on the conductivity of the films both in the lateral direction and in the direction normal to the substrate surface was studied. The initial Cu(In,Ga)Se$_2$ films with the Ga/(In + Ga) ratio in the range of 0.03–0.12 were obtained by thermal selenization process of stacked metallic precursors and by co-evaporation of all elements from various sources. The plasma treatment was carried out in a high-density low-pressure RF inductively coupled plasma reactor in argon plasma. The average ion energy was 200 eV, the processing time was 60 s. It is shown that the processes of the plasma nanostructuring of the Cu(In,Ga)Se$_2$ film surface lead to the formation of a thin modified near-surface layer with a resistivity of 2–3 orders of magnitude less than for the bulk of the film.

1. Introduction

Semiconductor polycrystalline copper indium gallium diselenide films Cu(In,Ga)Se$_2$ (CuIn$_{1-x}$Ga$_x$Se$_2$) are widely used in thin-film solar cells, which are reported to achieve the record solar cell conversion laboratory efficiency of 23.3% [1]. A promising direction for further increasing the efficiency of solar cells based on copper indium gallium diselenide films is the nanostructuring of their surface [2]. We have proposed methods for the effective nanostructuring of the Cu(In,Ga)Se$_2$ surface during the processing of the films in the high-density low-pressure RF inductively coupled argon plasma [3, 4]. As a result, arrays of vertical uniform nanostructures with lateral dimensions of 10–30 nm and a height of 10–90 nm, with a surface density of (0.8–1.8) × 10^{11} cm^{-2} were formed on the film surface (figure 1), while these geometrical parameters could be controlled by varying the modes of the plasma treatment. It is well known that the processes of thermal, laser, and radiation modification of Cu(In,Ga)Se$_2$ are capable of greatly changing the electrical properties of the films [5, 6]. Therefore, as a further step, it becomes necessary to investigate possible changes in the electrical properties of copper indium gallium diselenide films after the plasma nanostructuring. The aim of this work was to study the electrical conductivity of $CuIn_{1-x}Ga_xSe_2$ (x = 0.03–0.12) thin films in the lateral direction and in the direction normal to the substrate surface in the initial state and after the nanostructure array formation in plasma.

2. Experimental

The initial $Cu(In,Ga)Se_2$ thin films with the Ga/(In + Ga) ratio in the range of 0.03–0.12 were grown on glass substrates by thermal selenization process of stacked metallic precursors and by co-evaporation of all elements from various sources. The Cu/(In + Ga) ratio varied over the wide range of 0.67–2.37. The thickness of the films was 2.0–2.4 µm. The processes of the film growth are described in more detail in [3, 7]. The data on the chemical composition of the obtained films is given in table 1.

Table 1. Impact of the nanostructuring in plasma on the resistivity of the $Cu(In,Ga)Se_2$ thin films

Sample no.	Growth method	Ga/ (In+Ga)	Cu/ (In+Ga)	ρ_{init} Ohm cm	$\rho_{experim}$ Ohm cm	Petritz's model analysis	
						ρ_{surf} Ohm cm	ρ_{init}/ρ_{surf}
			Measurements in the lateral direction				
1	Selenization	0.03	0.67	2.2×10^3	1.4×10^1	2.0	1100
2	Selenization	0.07	0.66	9.1×10^2	4.3	4.7×10^{-1}	1936
3	Selenization	0.12	2.37	1.9	7.0×10^{-2}	1.0×10^{-2}	190
			Measurements in the direction normal to the surface				
4	Co-evaporation	0.10	0.93	8.0×10^2	2.6×10^2	–	–
5	Selenization	0.11	1.36	1.9×10^4	1.2×10^4	–	–

Experiments on the plasma treatment of the samples were carried out in a high-density low-pressure RF inductively coupled plasma reactor in argon plasma. The plasma discharge was ignited when the RF power of 800 W was applied from the inductor (frequency 13.56 MHz). An independent RF power of 300 W from an individual high-frequency generator was applied to the substrate holder, which provided the average energy of Ar^+ ions of about 200 eV. The processing duration was 60 seconds. Typical images of the pristine surface and of the array of the formed nanostructures, using the sample no. 3 (table 1) as an example, are shown in figure 1.

Measurements of the resistivity in the lateral direction were carried out using a four-probe method for the samples which had the $Cu(In,Ga)Se_2$ film deposited directly on a dielectric glass substrate. Measurements of the resistivity in the direction normal to the surface were carried out by obtaining the current-voltage characteristics of a $Mo/Cu(In,Ga)Se_2/Mo$ structure. In this case, the $CuIn_{1-x}Ga_xSe_2$ film was deposited on a glass substrate with a sublayer of molybdenum, and an ohmic molybdenum contact with an area of about 2 mm^2 was deposited with minimal heating (50 °C) on top of the grown film. The current-voltage characteristics of the $Mo/Cu(In,Ga)Se_2/Mo$ structures were strictly linear over a wide range of voltage bias, which allowed calculating the resistivity value using simple equations.

3. Results and discussion

Performed measurements of the resistivity of the films in the initial state ρ_{init} showed values in the range of 10^0–10^5 Ohm cm (table 1), corresponding to the wide range of resistivity values described in literature [6, 8], which, in the most general case, is determined by the grain sizes, the Cu/(In + Ga) ratio, the presence of pores, the formation of $Cu_{2-x}Se$ inclusions, etc. During the plasma treatment, a surface sputtering was observed, as a result of which the thickness of the films decreased by 100–200 nm and a partial alignment of the microrelief and a formation of nanostructures occurred (figure 1). The values of the resistivity of $Cu(In,Ga)Se_2$ after the plasma treatment $\rho_{experim}$, calculated under the assumption of uniformity of electrical properties along the film thickness, are listed in table 1.

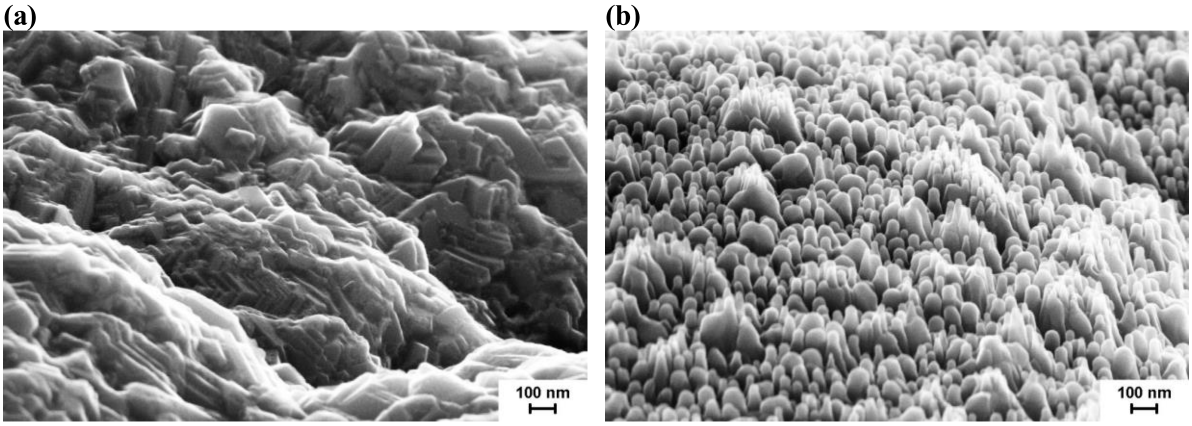

Figure 1. Electron microscopy images of the (a) initial and (b) nanostructured $Cu(In,Ga)Se_2$ film surfaces (shown for the sample no. 3).

A direct analysis of the data in table 1 shows that when the charge carriers flow in the lateral direction, the resistivity decreases sharply by about 2 orders of magnitude. This behaviour is typical for the modification of $Cu(In,Ga)Se_2$ films by rapid thermal annealing and laser processing [5, 6]. However, it should be noted that the electrical conductivity of the $Cu(In,Ga)Se_2$ films in the direction normal to the substrate varies insignificantly – by 1.6–3.1 times.

To explain the obtained experimental results, a model can be applied, according to which the plasma nanostructuring of the $Cu(In,Ga)Se_2$ thin films only modifies the electrical properties of the near-surface part of the films. From a physical point of view, there are no real reasons which, with fairly short-term and low-energy effect of Ar^+ ions, could change the structural and electrical properties of the films over the entire thickness of 2 μm. We presume that as a result of the plasma nanostructuring, a double-layered structure is formed (figure 2), when a layer with high electrical conductivity forms on the surface, and the rest of the bulk of the film does not change its electrical properties.

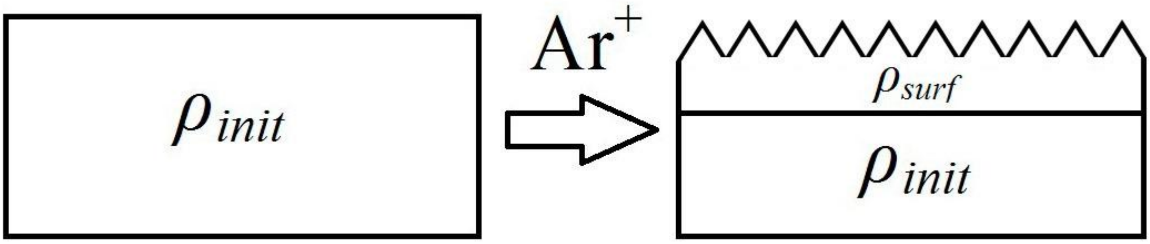

Figure 2. Schematic model of the formation of a double-layered structure of the $Cu(In,Ga)Se_2$ thin films during the plasma treatment.

The results of the calculations of the resistivity of a high-conductive surface layer ρ_{surf} using the mathematical equations of the Petritz's two-layer model [9] under the assumption of the thickness of the modified layer of 200 nm are presented in table 1. Analysis of these data shows that the resistivity of the near-surface layer decreases by 2–3 orders of magnitude, and the minimal changes are typical for the films which initially had high electrical conductivity. The explanation of the decrease in the resistivity of the near-surface layer during the plasma treatment is complex in nature, and includes an increase in the concentration of charge carriers due to radiation defects, the appearance of conductive inclusions on the surface, the filling of voids between the grains due to redeposition effects, etc.

When analyzing the experimental results for the current flowing along the normal to the substrate surface, another contradiction arises: the appearance of a thin near-surface layer can not quantitatively explain the observed decrease in the resistivity by 1.6–3.1 times. In this situation, additional phenomena should be taken into account:

- a possible increase of the upper electrode area due to additional carrier spreading in the low-resistance near-surface layer;
- an increase in the effective surface area of the upper Mo/Cu(In,Ga)Se_2 electrode as a result of the surface nanostructuring. Estimates show that for the actual geometrical parameters of the nanostructures obtained after a 60 s plasma treatment, the effective surface area of the electrode can increase by 1.5–4.0 times. Therefore, to explain the changes in the conductivity in the direction normal to the film, it is necessary to take into account not only the formation of a near-surface layer during the nanostructuring in plasma, but also the increase in the actual electrode surface area.

4. Conclusions

The results of these investigations show that the processes of the plasma nanostructuring of the surface of Cu(In,Ga)Se_2 thin films lead to the formation of a thin modified near-surface layer with a resistivity of 2–3 orders of magnitude less than for the bulk of the film. The presence of this layer should change the parameters of the current-voltage characteristics of the ZnO/CdS/Cu(In,Ga)Se_2/Mo solar cell structure. Our next research will be devoted to the measurements of the current-voltage characteristics of the solar cells with nanostructured Cu(In,Ga)Se_2 layers.

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