New plasma-assisted approach to the fabrication of Cu(In,Ga)(S,Se)₂ nanowires

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Abstract. In this work we have applied the low-energy high-density low-pressure radio-frequency inductively coupled argon plasma treatment to the Cu(In,Ga)(S,Se)₂ thin films grown on glass substrates using a selenization/sulfurization process. This approach allowed to obtain nanowires with an average height varying from 120 to 240 nm and with a 15-50 nm diameter. It is shown that the mechanism of the nanowire formation is plasma-assisted vapor-liquid-solid growth in combination with micromasking with In-Ga alloy nanoinclusions serving both as catalyst droplets and micromasks.

1. Introduction
Chalcopyrite compounds Cu(In,Ga)Se₂ (CIGS) and Cu(In,Ga)(S,Se)₂ (CIGSS) are promising materials for the fabrication of high-efficient thin film solar cell devices due to the unique combination of a high absorption coefficient, stability, radiation tolerance and a tunable direct band gap in the range from 1.04 eV for CuInSe₂ to 2.4 eV for CuGaS₂ [1, 2]. CIGSS-based thin film solar cells are reported to show an outstanding efficiency reaching 20.9% [3]. One of the most promising methods to further increase the solar cell efficiency is to apply a micro- or nanostructured absorbing CIGS/CIGSS layer. While it was reported to be fabricated using high-energy ion beam sputtering [4], we have proposed a novel, more versatile and technologically convenient approach of using low-energy inductively coupled plasma treatment which allowed us to carry out plasma-assisted formation of arrays of uniform nanotips with controlled geometrical parameters on the surface of CIGS layers [5, 6].

Here we apply this approach to CIGSS films and report the plasma-assisted fabrication of nanowires with varied height, diameter and density during inductively coupled argon plasma treatment of CIGSS films grown using a selenization/sulfurization growth method.

2. Experimental details
Cu(In,Ga)(S,Se)₂ thin films with a 2.5 μm thickness were grown on glass substrates using a selenization/sulfurization process. This method is based on simultaneous annealing of the metal layers in the combined Se and S vapor in an inert gas stream [2]. For the film growth, precursor Cu-In-Ga
films were deposited onto glass substrates at 100°C by ion-beam plasma evaporation. The simultaneous selenization and sulfurization were conducted in a horizontal tube reactor under N₂ flow as a reaction with solid state sources of S and Se and had two consecutive annealing stages at 260°C and 540°C temperatures [2]. For the films, the Ga/(In+Ga) and S/(Se+S) ratios were 0.07 and 0.77, respectively.

Plasma treatment of the samples was carried out in a high-density low-pressure radio-frequency inductively coupled argon plasma reactor according to our experimental technique used for the nanostructuring of CIGS films [5, 6]. During the treatment, the argon gas flow was 10 sccm, the operating pressure was 0.07 Pa, and the RF bias power on the aluminum substrate holder was 300 W. These plasma reactor operating parameters allowed obtaining the low average energy of the bombarding argon ions of about 200 eV. The treatment duration was 60 s and 120 s.

The morphology of the as-grown and plasma-treated CIGSS film surface was studied with scanning electron microscopy (SEM) using a Supra 40 (Carl Zeiss) microscope.

3. Results and discussion

As-grown CIGSS films were polycrystalline, which is also typical for CIGS films [5, 6]. SEM images of the initial surface of the CIGSS thin film on a glass substrate are given in figure 1. On the CIGSS film surface, there were droplet-like spherical polycrystalline clusters of 1–3 μm size, as seen in figure 1(a), which were resulted from the used film growth technique. The grain size, as measured on flat surface areas such as shown in figure 1(b), was 65–220 nm. According to the high-resolution SEM data, the initial film surface also showed a presence of arrays of nanosize (5–15 nm) inclusions with a density of 1.5×10¹² cm⁻², as seen in figure 1(b) as white dots. In Ref. [7] it was theoretically shown for the CIGS material that there should take place the segregation of Ga or In nanoinclusions, and it is expectable to have them also for the CIGSS films. Therefore, the nanoinclusions on the initial surface are assumed to be metallic In, Ga or In-Ga alloy nanoparticles.

![Figure 1. SEM images of the initial CIGSS film surface.](image)

Plasma treatment of the CIGSS film surface resulted in its significant modification. While the spherical clusters remained practically intact, the grain-related micro-relief on flat areas was smoothed. Simultaneously, there also took place a formation of vertical nanostructures uniformly distributed over the entire plasma-treated area including spherical clusters (figure 2). After the plasma treatment of 60 s duration, the average height of the nanostructures was 120 nm, the diameter was 15–35 nm, and the density was 8×10¹⁰ cm⁻². After the plasma treatment of 120 s duration, the average
height of the nanostructures was 240 nm, the diameter was 30–50 nm, and the density was $4 \times 10^{10} \text{ cm}^{-2}$. Typical SEM images for the nanowires formed on the CIGSS surface after the 60 s and 120 s plasma treatments are given in figure 3 and figure 4, respectively. SEM data clearly show that the nanowires are characterized by round “caps” on their tops.

In order to explain the physical mechanism of the nanowire formation, we have to examine the main processes which take place on the surface of the CIGSS film during the plasma treatment. Firstly, a physical sputtering of film by low-energy Ar ions takes place. The surface is smoothed, and the sputtered atoms of selenium, sulfur, copper, indium, and gallium are distributed over it in a vapor phase. Secondly, plasma heats the film surface (up to ~500 K). The In-Ga nanoinclusions with eutectic temperature of $15.3 \, ^\circ \text{C}$ become liquid. As a result, the formation of In-Ga droplets, which are liquid during plasma treatment, occurs. These solidified droplets can be seen as “caps” on tops of the nanowires (figure 3, figure 4).

**Figure 2.** Top-down SEM image of the array of nanowires fabricated on the CIGSS film surface after a 60 s argon plasma treatment. A spherical cluster can be seen in the bottom-left corner of the image.

**Figure 3.** SEM image of the nanowires fabricated on the CIGSS film surface after a 60 s argon plasma treatment. Sample tilt during imaging is 70°.
During the plasma treatment the droplets serve as micromasks protecting the material under it from physical sputtering. On the other hand, when the high surface temperature and the high vapor density for the sputtered atoms provide sufficient conditions for the realization of vapor-liquid-solid growth [8], the droplets serve as liquid catalysts for the growth of solid nanowires under them. As a result, the nanowires can grow both in vertical direction and laterally with the ongoing treatment, which corresponds to the SEM data. The density decrease can be explained by eventual removal of the micromasks.

Figure 4. SEM image of the nanowires fabricated on the CIGSS film surface after a 120 s argon plasma treatment. Sample tilt during imaging is 70°.

4. Conclusions
We have experimentally shown a capability of fabricating large arrays of Cu(In,Ga)(S,Se)₂ nanowires with varied geometrical parameters using low-energy plasma treatment of thin films on glass substrates. The physical mechanism of CIGSS nanowire growth includes micromasking and the vapor-liquid-solid mechanism with In-Ga nanoinclusions serving both as micromasks and catalytic liquid droplets. Our approach is versatile, low-cost, applicable both to CIGSS and CIGS films, and is prospective for the development of thin film photovoltaic devices with high efficiency.

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