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Nanostructuring of the CIGS Films Surface by the Plasma Treatment with Low Ion Energy

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We report on surface nanostructuring of $Cu(In,Ga)Se_2$ (CIGS) films using inductively coupled argon plasma treatment with the ion energy of 25–30 eV within 30–120 s. The films were fabricated on glass substrates using the selenization method and had a polycrystalline structure. We demonstrate that the plasma treatment results in the formation of tip-shaped nanostructure arrays with the geometrical parameters controlled by the treatment duration. The features of the surface nanostructuring using low energy ions are discussed.

Keywords: CIGS films; selenization; plasma treatment; nanostructuring.

1. Introduction

Nanostructuring of CIGS films used in photovoltaic systems is a prospective field of research. Recently, we have proposed a new method for effective nanostructuring of CIGS films based on their surface treatment in the high-density low-pressure inductively coupled argon plasma.[1,2] This method resulted in the formation of arrays of conical and

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cylindrical tip-shaped nanostructures with the density of $\sim 10^{11}\,\mathrm{cm}^{-2}$ and height of 10–90 nm on the treated surface. The applied average argon ion energy was 200 eV, which allowed fabricating nanostructures with controlled geometrical parameters using short plasma treatment (10–60 s). However, this process was accompanied by removal of the surface layer of 100–200 nm thickness.[1] For further investigation of capabilities of this method, it became prospective to study nanostructuring of CIGS film surface with low energy argon ions in order to reduce the material removal and to preserve its structure. In this way, we investigated the nanostructure array formation of the CIGS films through the plasma treatment with low average argon ion energy of 25–30 eV.

2. Experimental

Glass/CIGS film systems were used as initial structures in which CIGS thin films were grown using the selenization method.[1,3] For the as-grown films, the Ga/(In+Ga) ratio was 0.24, the Cu/(In+Ga) ratio was 1.23, and the Se/(In+Ga+Cu) ratio was 0.97.

Plasma treatment of the films was carried out in a high-density low-pressure radiofrequency inductively coupled plasma (RF ICP, 13.56 MHz) reactor.[1,2] We used inert argon gas for the plasma discharge. The reactor chamber pumping out was performed using a turbomolecular pump. The residual pressure was 2×10^{-6} Torr. Experiments were carried out with the following parameters: the inductive RF power — 800 W; the argon gas flow — 10 sccm; the operating argon gas pressure — 0.07 Pa; the RF bias power on the substrate holder — 0 W. Without RF bias, the average argon ion energy was 25–30 eV. The treatment duration was 30–120 s.

The film morphology was studied with scanning electron microscopy (SEM) using a Supra 40 microscope. The film composition was obtained with energy dispersive X-ray (EDX) analysis using a INCAx-act spectrometer.

3. Results

The SEM study shows that CIGS films are polycrystalline, which is typical for such films grown on glass substrates using the selenization method.[1,3] A typical image of the as-grown CIGS film surface is shown in Fig. 1. The films consisted of large grains with edges oriented along the crystallographic directions. Lateral sizes of the grains are 380–920 nm and their height above the surface attains 370 nm. The surface density of the grains is $6 \times 10^7\,\mathrm{cm}^{-2}$. Large grains contacted with smaller round grains observed on their flat areas with 25 nm average size and the density of $\sim 10^{10}\,\mathrm{cm}^{-2}$.

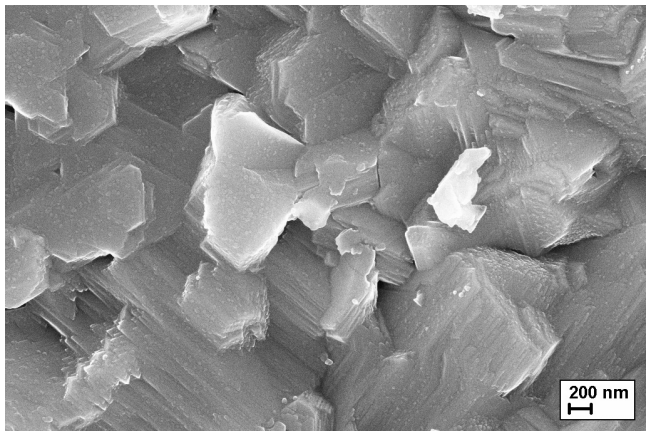

Fig. 1. SEM image of the as-grown CIGS film surface.

For the films after RF ICP treatment, the overall granular microrelief morphology was still present due to low physical sputtering. Formation of array of practically homogeneous nanostructures distributed uniformly on the surface takes place. A typical image of the CIGS film after 120 s plasma treatment is shown in Fig. 2. Cylindrical and tip-shaped nanostructures were formed.

The plasma treatment duration has a direct impact on the nanostructure geometrical parameters. Upon 30 s their density was $2 \times 10^{11}\,\mathrm{cm}^{-2}$, average lateral size and height were 17 nm and 45 nm,

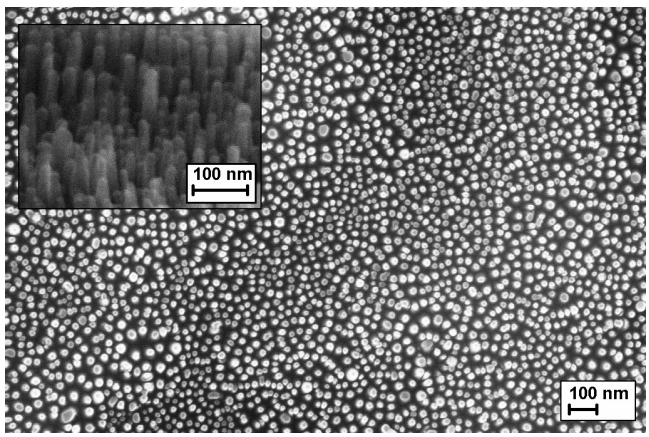

Fig. 2. SEM image of the nanostructured CIGS film surface after 120 s RF ICP treatment. The inset shows the surface inclined at 70°.

respectively. For the 120 s duration, their density was $1 \times 10^{11}\,\mathrm{cm}^{-2}$, average lateral size and height were 25 nm and 100 nm, respectively. The EDX data showed an increase of Ga content by more than 9 at.% at the nanostructured surface, indicating that gallium may serve as a catalyst for vapor–liquid–solid growth or as a micromask.[1]

4. Conclusion

The results of this work show that for the average ion energy reduced to 25–30 eV, the surface nanostructuring processes still take place. While the nanotip array formation is similar to the case of 200 eV ion energy, there are new features. First, due to the reduced physical sputtering, the material removal is much less. Secondly, due to the lower intensity of the sputtering and redeposition processes, the nanostructuring process is slower than for the 200 eV ion energy. It results in the smoother variation of the nanotip parameters with the treatment duration variation and allows the precise control during their formation.

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