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Femtosecond Laser Crystallization for Boosting the Conversion Efficiency of Flexible Ink-Printing $Cu(In,Ga)Se_2$ Thin Film Solar Cells

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Abstract

In this work, the effects of femtosecond laser annealing (fs LA) process on the structural and optoelectronic properties of the non-vacuum nanoparticle printing $Cu(In,Ga)Se_2$ (CIGS) thin films were systematically investigated. A near 20% enhancement in photovoltaic conversion efficiency was achieved.

1. Introduction

The ink-printing method is a desirable approach for fabricating large-scale flexible $Cu(In,Ga)Se_2$ (CIGS) thin-film photovoltaics (TFPV) devices because of its potential for rapid process, mass production and low-cost non-vacuum device fabrication. However, the reliability has been one of the most cumbersome obstacles toward promoting ink-printing CIGS TFPV, because of the abundance of unwanted defects and relatively poor film crystallinity inherent to this non-vacuum deposition process.

In this work, the effects of femtosecond laser annealing (fs-LA) treatment on the structural and optoelectronic properties of the ink-printing CIGS thin films were investigated. It was observed that, while the film surface morphology remains essentially unchanged under superheating, both the crystalline structure and defects reduction were significantly improved after the fs-LA treatment.

2. General Instructions

Figure 1(a) shows a schematic diagram of the fs-LA system used in this study. The CIGS thin films fabricated by the non-vacuum nanoparticle printing process were placed on a three-axis translation stage for adjusting the location. For comparison purposes, a KrF excimer laser (wavelength = 248 nm, pulse width = 20 ns) and a Ti:sapphire mode-locked laser (wavelength =800 nm, pulse width = 100 fs) were used as the light sources for the LA process. Figures 1(b) to 1(d) shows the surface morphologies of the CIGS thin films before and after different LA processing conditions. It is apparent that the surface morphology of the film treated with ns-excimer laser (Fig. 1(c)) exhibits the typical feature of melting, while that of the fs-LA film (Fig. 1(d)) remains nearly intact as compared to that of the as-deposited CIGS films.

The chalcopyrite CIGS crystalline structures, the Raman signal of A_1 mode, the stoichiometric composition, and the ultrafast carrier relaxation time were examined by X-ray diffraction (XRD), Raman, Energy Dispersive Spectroscopy (EDS) and ultrafast pump-probe measurements, respectively, to study the effects of fs-LA treatment. The results indicate that the smallest FWHM of the (112) peak, the best stoichiometric composition and longest defect-related carrier lifetime are obtained with an optimized fs-LA fluence of ~6.8 mJ/cm^2 and scanning rate of 30 mm/s[1,2]. Moreover, under the optimal fs-LA processes, the defect states of In_{Se}, V_{Se}, and In_{Cu} were all reduced to vanishing level, which have been elaborately verified by analyzing the photoluminescence (PL) spectra.

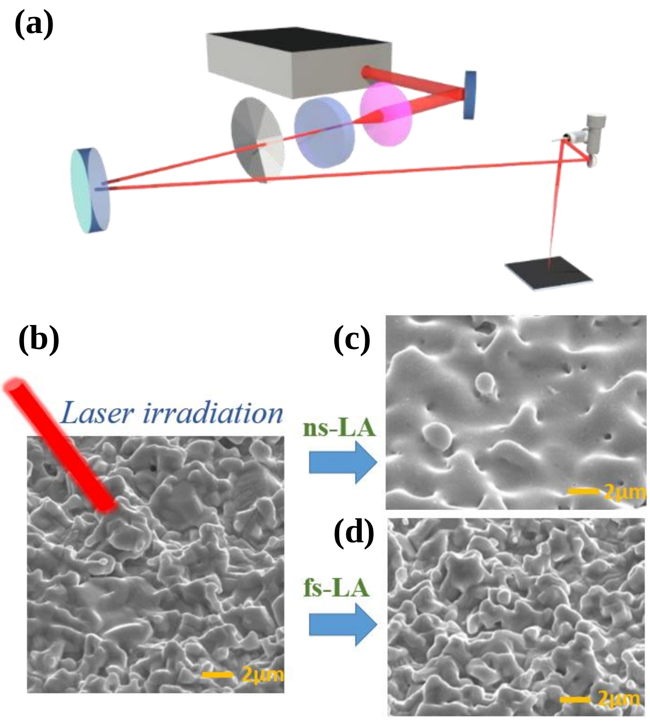

Fig.1.(a) Schematic diagram of fs-LA system. Surface morphologies of CIGS thin films before (b) and after different pulsed laser treatment using (c) KrF excimer laser (ns-LA) and (d) Ti:sapphire mode-locked laser (fs-LA), respectively.

In order to further investigate the defect states in the present CIGS films, the temperature and power-dependent PL spectra were measured. Figures 2(a)-2(d) show the PL spectra obtained in the temperature range of 10~80 K and power range of 0.5-5 mW for the as-deposited and fs-LA treated CIGS films, respectively. Each curve in the figure can be fitted by Gaussian profiles and four primary peaks P1-P4 were found. The typical results for the as-deposited and fs-LA treated CIGS films measured at 10 K and 5 mW are shown in Figures 3(a) and 3(b), respectively.

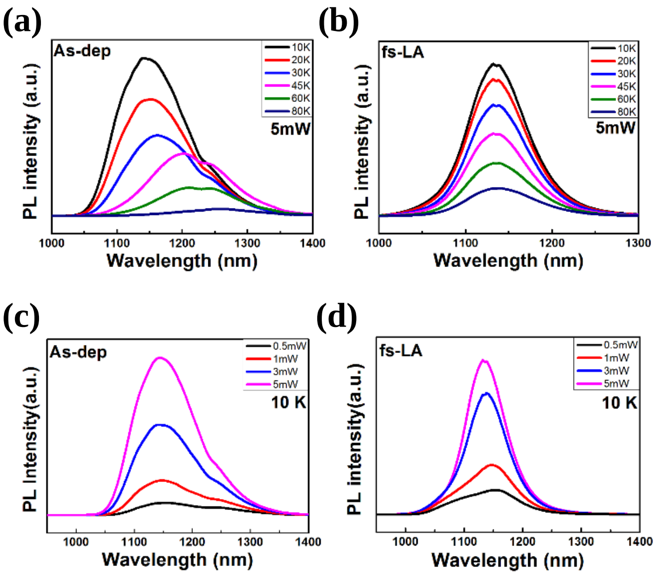

Fig.2. Power-dependent PL spectra of CIGS films (a) before and (b) after the fs-LA treatment in the temperature ranges between 10−80 K, respectively. Temperature-dependent PL spectra of CIGS films (c) before and (d) after the fs-LA treatment in the power ranges between 0.5−5 mW, respectively.

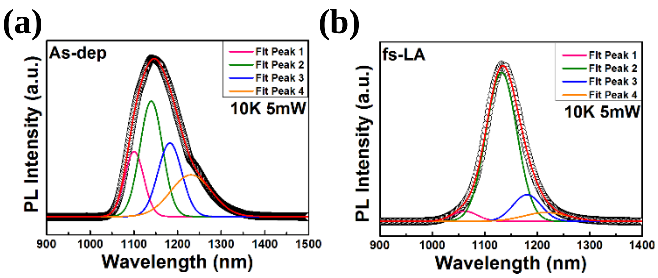

Fig.3. The experimental data of a typical PL spectra (measured at 10 K and 5 mW) and the Gaussian fitting for (a) as-deposited and (b) fs-LA CIGS films. The identified defects, corresponding to In_{Se}, V_{Se}, and In_{Cu} for P1, P3 and P4, respectively.

According to the correlations between the peak shift, temperature and exciting power, the four primary peaks used in the fitting process can be assigned as follows. Namely, P2 is related to band-to-band transition, while P1, P3 and P4 are all related to donor–acceptor pair (DAP) transitions[3,4]. Values of the activation energy (E_a) related to these peaks using the Arrhenius equation[5] were obtained and the identified defects, corresponding to In_{Se}, V_{Se}, and In_{Cu} for P1, P3 and P4, respectively[6]. It is also interesting to note that, in comparison to the PL spectra obtained for the as-deposited CIGS film, The magnitude of P1 and P4 peaks in the fs-LA CIGS film are both reduced greatly (Figure 3(b)), suggesting that the In_{Se} and In_{Cu} defects have been almost completely eliminated by fs-LA.A typical CIGS TFPV device with as-deposited or fs-LA annealed CIGS thin films were fabricated. The modification in chalcopyrite structure and stoichiometric composition via the fs-LA treatment greatly decreases the shut leakage current and recombination centers, resulting in a near 20% enhancement in photovoltaic conversion efficiency.

3. Conclusions

In summary, the fs-LA treatment of the ink-printing CIGS thin films has evidently exhibited the following features: (1) There is no melting effect, which cannot be achieved via other annealing processes. (2) Preferably enhancing the quality of crystallinity in (112)-preferred orientation. (3) Reducing the phenomenon of indium segregation with an optimized laser scanning rate. (4) Decreasing the defect states of In_{Se}, V_{Se}, and In_{Cu}, verified by temperature and power dependent PL measurements. (5) Modifying shut leakage current and ideal factor in devices, resulting in a much better performance. These results have convincingly illustrated that the fs-LA treatment is a promising way to achieve the high conversion efficiency in flexible non-vacuum CIGS thin film photovoltaic devices.

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