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Intrinsic stoichiometry optimization of polycrystalline lead selenide film in the sensitization process by iodine concentration regulation

Hao Yang *, Lei Chen, Xiaojiang Li, Jianbang Zheng

Shaanxi Key Laboratory of Optical Information Technology, School of Science, Northwestern Polytechnical University, Xi'an 710072, China

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ABSTRACT

The stoichiometry influence of polycrystalline lead selenide material on crystalline structure and photoelectric properties was demonstrated. The responsivity of 3.97 A/W was achieved biased at 4 V with the optimal iodine molecular density of 9.1×10^{11} mm^{-3} and oxygen pressure of ~0.15 MPa in the sensitization process. The photoelectric performance can be further enhanced with iodine at low iodine molecular density of $<1.5\times10^{12}$ mm^{-3}. It is revealed that a serious deviation of Pb/Se atomic ratio from 1:1 is responsible for the significant decline of responsivity due to over-iodination in the sensitization process. It is helpful to understand the roles of iodine and oxygen in the sensitization of lead salt materials.

1. Introduction

Lead selenide (PbSe) is a marvelous narrow gap semiconductor for the thermoelectric [1–3], infrared emitting [4,5] and photodetection applications [6–10]. Particularly, the PbSe low-dimensional compounds are also very promising for the infrared photoinduced nonlinear optical effects [11]. Recently, the uncooled polycrystalline PbSe photodetectors in the mid-infrared spectral range (2–5 μm) have attracted wide attention in many fields such as laser welding monitoring, environmental monitoring, and biomedical diagnosis, etc [7–10]. With this technology, the photodetection at room temperature (298 K) can be achieved due to the enhanced photoelectric performance. This technology generally contains the film fabrication by vapor phase deposition (VPD) compatible with CMOS readout electronics, and a sensitizing process for doping of oxygen and iodine at specified temperature [12–17]. The sensitization process should be affected by the as-deposited crystalline structure, the atmosphere concentration, the temperature and time used [12–15]. The specified carrier transportation structure may be constructed between the polycrystalline grains with specified stoichiometry during the sensitization process, thus the minority carrier lifetime should be significantly increased [16,17]. In the recent years, the sensitization methods reported in the previous works focused on the iodine and oxygen diffusion technology to construct the optimal stoichiometry essentially [12–15]. However, the stoichiometry influence of polycrystalline PbSe material on the photoelectric properties and the crystalline structure is still unclear.

In this paper, we experimentally verified that the stoichiometry deviation of PbSe microcrystal can affect the photoelectric performance of PbSe photoconductors significantly, for the first time as we know. The crystalline structures and photoelectric properties were characterized for samples sensitized at different iodine concentrations. It is revealed that the photoelectric performance can be further enhanced only at low iodine dose.

2. Experiments

The PbSe films were fabricated by VPD technology on the Si (100) substrate at vacuum degree of $<10^{-6}$ Torr with 120 °C substrate temperature and 3 Å/s deposition rate. The thickness of as-deposited film was 1 μm. The Hall measurements show that the as-grown samples deposited at room temperature are p-type with $p=1.4980\times10^{18}$ cm^{-3}, and the as-grown samples deposited at high temperature of >120 °C are n-type with $n=5.5477\times10^{17}$ cm^{-3}, respectively. These films were then sensitized with different iodine molecular densities during the following stages: (1) annealed in I_2 and O_2 hybrid atmosphere at 220 °C for 15 min, (2) annealed in O_2 at 450 °C for 1 h. The stoichiometry of PbSe microcrystal was changed by the iodine

* Corresponding author.
E-mail address: yhao@nwpu.edu.cn (H. Yang).

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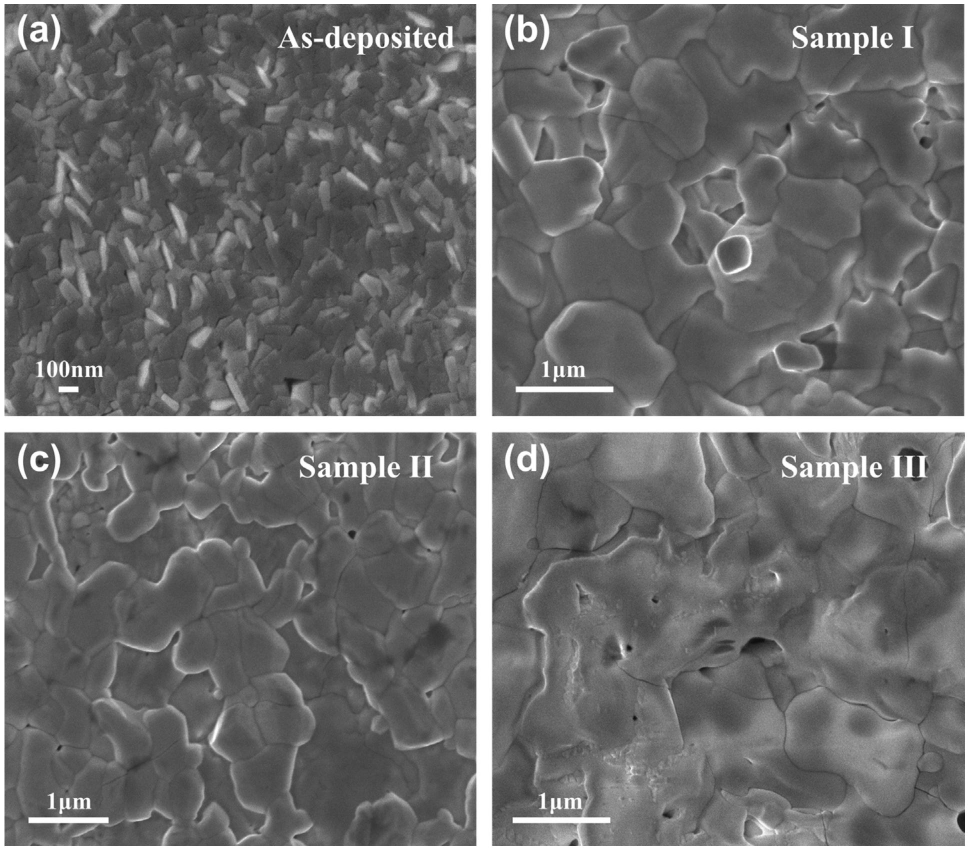

Fig. 1. SEM morphologies for (a) as-deposited film fabricated at 120 °C substrate temperature and $< 10^{-6}$ Torr vacuum degree, and samples sensitized with iodine molecular density of (b) 3.0×10^{11} mm^{-3}, (c) 9.0×10^{11} mm^{-3} and (d) 1.5×10^{12} mm^{-3}, respectively.

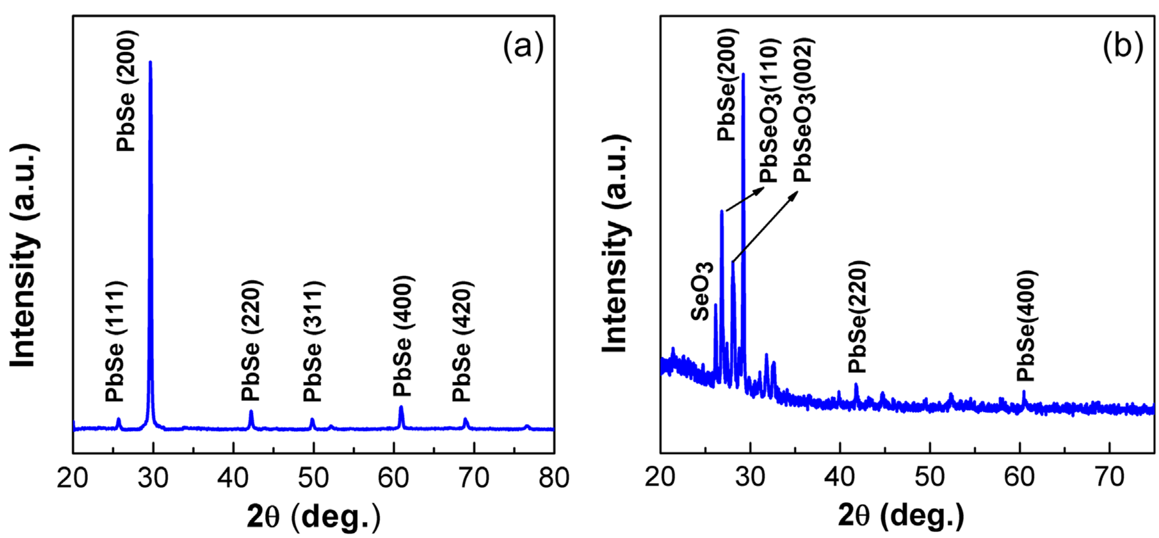

Fig. 2. XRD patterns of (a) as-grown film with deposition rate of 3 Å/s and substrate temperature of 120 °C, and (b) sample II sensitized in $I_2 + O_2$ at 220 °C then in O_2 at 450 °C with iodine molecular density of 9.0×10^{11} mm^{-3} in the first sensitization stage.

concentration regulation in the sensitization process. The sensitized polycrystalline films were labeled as samples I–V corresponding to iodine concentrations of 3.0×10^{11}, 9.0×10^{11}, 1.5×10^{12}, 2.1×10^{12} and 3.3×10^{12} mm^{-3}, respectively. X-ray diffraction (XRD) was performed using Cu-Kα radiation ($\lambda = 1.5418$ Å) with a 2θ scan range of 20–80°. X-ray Photoelectron Spectroscopy (XPS) measurement was carried out to reveal the surface composition of PbSe microcrystal. The atomic proportions were calculated by XPS data. The carrier concentration and mobility of samples were achieved by Hall measurements at 3000 G. The photoelectric properties were measured using Newport 63938 mid-infrared source and Agilent 2912A DC supply meter with 55.39 mW incident mid-IR radiation peaking at 4 µm. Multiple samples were fabricated to be the sample group using a specified iodine concentration to construct one experimental data point. The final experimental data was the