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Growth of γ-In_2Se_3 films on Si substrates by metal-organic chemical vapor deposition with different temperatures

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Abstract

In_2Se_3 films were deposited on the p^+-Si(1 1 1) substrates by metal-organic chemical vapor deposition (MOCVD) for the first time at temperatures higher than 500 °C. Trimethyl indium (TMI) and H_2Se were used as the source reactants with the flow ratio of [H_2Se]/[TMI] being maintained at 6.7. The growth temperature was varied from 350 to 650 °C. Powder X-ray diffraction analyses revealed that the In_2Se_3 film grown is polycrystalline and has a wurtzite structure when the growth temperature is below 450 °C. Instead, a rhombohedral structure began to appear when the growth temperature is above 450 °C. Besides, SEM observations indicated a surface morphology of columnar structure for all films grown. Optical properties were examined by photoluminescence (PL) measurements. It was found that by conducting the growth at 550 °C a strong PL emission at around 2.14 eV was observed at 20 K. The luminescence mechanism was found to be dominated by the free excitons based on the temperature-dependent PL spectra from 20 to 120 K. However, bound exciton emissions were also observed or even became the dominant band when the films were grown at temperatures lower than 500 °C. Otherwise, the intensity of the 2.14 eV peak reduced greatly when the growth temperature was higher than 550 °C. Power-dependent PL measurements with excitation power varying from 0.1 to 100 mW confirm the luminescent mechanism and the material quality of the film grown at 550 °C. It is concluded that single-phase γ-In_2Se_3 films can be achieved at temperatures lower than 450 °C; however, good-quality In_2Se_3 films with the simultaneous appearance of γ- and β-phase structures can be grown at around 550 °C.

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1. Introduction

Indium Selenide (In_2Se_3) is a very special material because it can present five different phases including α, β, γ, κ and δ phases. Among these phases, α and β phases have further structures, namely hexagon and rhombohedron structures [1]. There are only two basic phases: one is the layered structure called α-phase, another is the defect structure of In_2Se_3 called γ-phase. In an early study, a stable layered structure (α-In_2Se_3) was defined [2]. It has a five-layers arrangement of Se–In–Se–In–Se linked by weak van der Waals force with a stacking sequence of ABC [3]. β-In_2Se_3 is a metastable structure obtained by heating α-In_2Se_3 and it will transform back to α-In_2Se_3 at room temperature unless it is doped with Sb, which makes it stable even though the heating is terminated [4]. γ-In_2Se_3 is a defective wurtzite structure, and in order to satisfy the octet rule for sp^3, one-third of the sites are vacant and form screw arrays along the *c*-axis [5]. The metastable anisotropic structure of κ-In_2Se_3 was obtained on the surface of γ-In_2Se_3 after it had been annealed. This structure is

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different from γ-In_2Se_3 but is similar to α-In_2Se_3 [6]. Some group has doped Zn to stabilize κ-In_2Se_3 [7]. Finally, δ-In_2Se_3 has not been treated till now. To the authors' knowledge, it can be obtained at high temperature and shows hexagonal structure.

In the field of electronic devices, In_2Se_3 is very suitable to be used for PRAM [8] due to its phase-change characteristics. Alternatively, in the field of optical devices, In_2Se_3 is very suitable to be used for solar cells [9]. This is because In_2Se_3 has a low surface recombination rate resulting from its low density of dangling bonds on the surface and also a high absorption coefficient for the whole solar spectrum. If $CuInSe_2$ (CIS) is used as the active layer for solar cell, In_2Se_3 could also be a good buffer layer since In_2Se_3 can structurally match well with CIS [10]. Up to now, many methods have been used to grow In_2Se_3 thin films, popular ones such as evaporation [11], molecular beam epitaxy (MBE) [12], or metal-organic chemical vapor deposition (MOCVD) [13] can be given. We have fabricated the In_2Se_3 films on the silicon (1 1 1) substrates by MOCVD using trimethyl indium (TMI) and H_2Se reactants. In our previous article we reported that the crystalline quality and surface morphology of single-phase γ-In_2Se_3 films can be improved by introducing an AlN buffer layer [14]. In this work, we examine the phase change of In_2Se_3 films grown on the silicon (1 1 1) substrates at different temperatures and resolve an optimal temperature to fabricate In_2Se_3 film on the Si (1 1 1) substrate by MOCVD.

2. Experimental procedure

In_2Se_3 thin films were prepared by a homemade atmospheric pressure MOCVD system. The growth chamber is a water-cooled vertical reactor. The substrate susceptor is

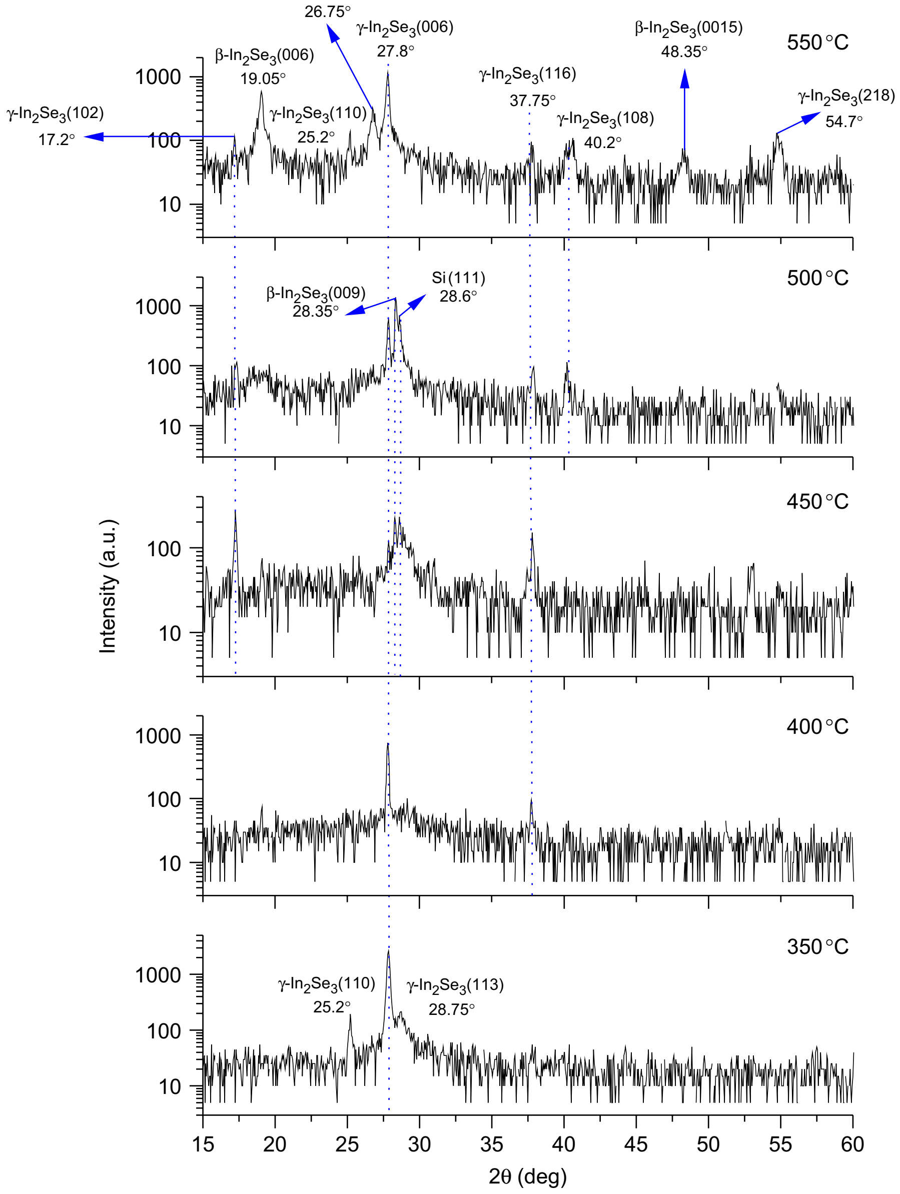

Fig. 1. XRD patterns of In_2Se_3 films grown on the Si (1 1 1) substrates at 350, 400, 450, 500 and 550 °C, respectively.

made of graphite, of 2 in diameter and coated with a SiC film on the top surface by CVD technique. The 4 cm × 4 cm substrates used were cut from a 6-in p-type vicinal (1 1 1) oriented Si wafer. Before loading, the substrate was etched by boiling it in H_2SO_4:H_2O_2 = 3:1 at 80 °C for 15 min and then dipped in HF solution (HF:H_2O = 1:10) for 15 s to remove native oxide formed on the surface. After loading, an In_2Se_3 film was grown at 200 °C for 10 min to form a buffer layer. TMI ($In(CH_3)_3$) and H_2Se were used as the sources of In and Se, respectively, and N_2 was used as the carrier gas. The use of multiple sources can change the ratio of VI–III (denoted by $R = [Se]/[In]$) arbitrarily and in this study the value of R was kept at 6.7 for all the crystal growth. Finally, top In_2Se_3 films were grown at temperatures varying from 350 to 650 °C for 40 min to obtain a thickness of about 500 nm.

The crystalline structure of films was evaluated by powder X-ray diffraction (XRD) using Cu K_α line as the X-ray source ($\lambda = 1.54056$ Å). The surface morphology of In_2Se_3 films was observed by scanning electron microscopy (SEM). The optical properties were investigated by photoluminescence (PL) measurements performed at 20–300 K. PL spectra were excited with the 488 nm line of an Ar laser at an excitation power of 0.1–100 mW. The luminescence was dispersed by a 0.5 m monochromator and detected by a water-cooled GaAs photomultiplier.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of In_2Se_3 thin films grown on the p^+-Si (1 1 1) substrates at different temperatures. Obviously the XRD patterns for all the

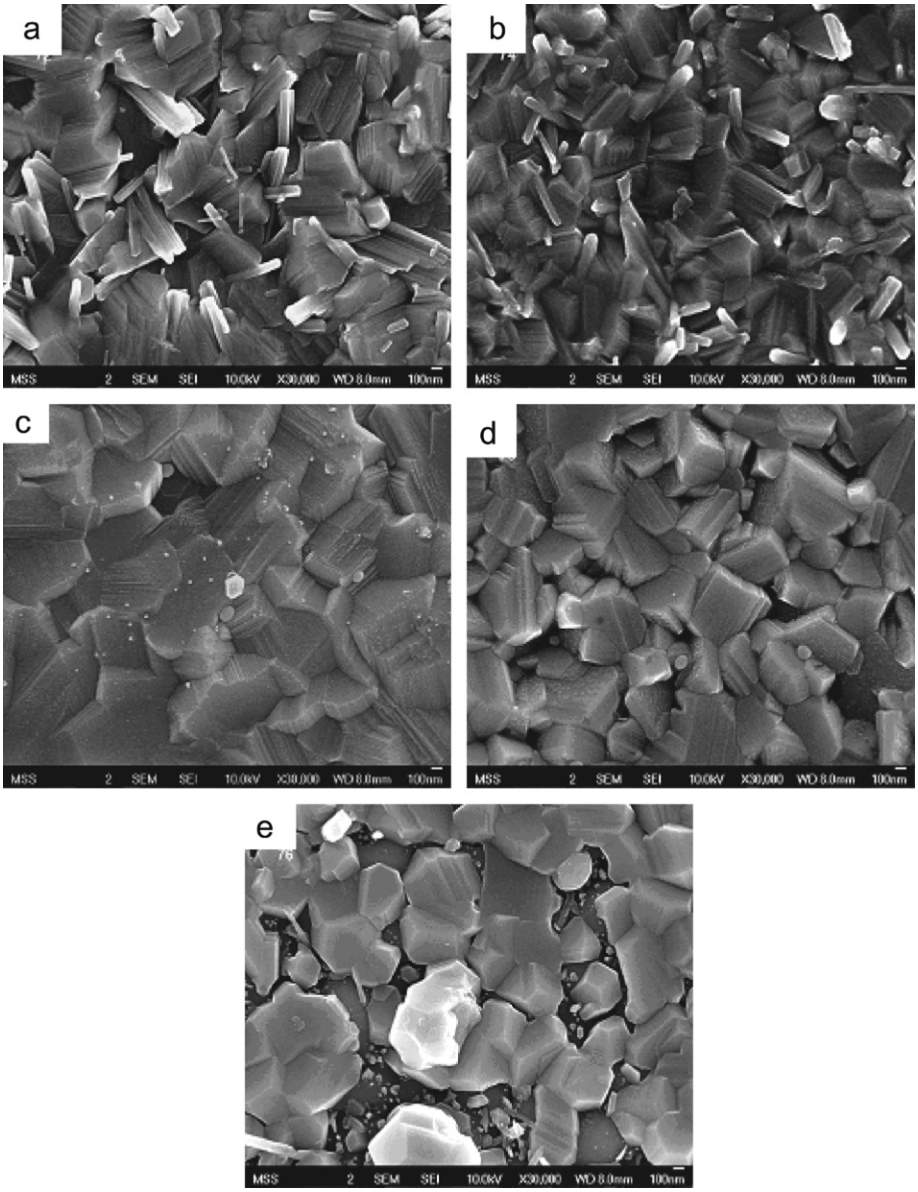

Fig. 2. Top-view SEM images of In_2Se_3 films grown on the Si substrates at (a) 350, (b) 400, (c) 450, (d) 500 and (e) 550 °C.

grown films have a main peak at $2\theta = 27.8^\circ$, which is identified as γ-In_2Se_3 (0 0 6) by the Joint Committee on powder diffraction standards [15]. Besides, there is the presence of (1 1 x) and (0 0 6) planes when the growth temperature is below 450 °C. Although the peak of γ-In_2Se_3 (0 0 6) could always be observed for the films grown, it did not mean that these films are all completely c-axis oriented. The γ-In_2Se_3 (0 0 6) is just an energetically stable plane, which dominates the appearance of the In_2Se_3 film surface. Once the growth temperature was over 450 °C, more peaks appeared in the corresponding XRD spectra. A higher energy given to the adatoms has made them arrange themselves to form some substrate planes. This means that the crystalline structure becomes more and more complicated and results in the growth in different directions. Ohtsuka et al. [16] had offered the phase diagram which shows a similar tendency to our specimens grown at 350–550 °C with $R = 6.7$. Clearly, the growth temperature of 450 °C is critical for the change of crystal structure. When the In_2Se_3 film was grown at a temperature lower than 450 °C, the film exhibited pure γ-phase structure. Then β-In_2Se_3 (0 0 X) phases began to appear when the film was grown at higher than 450 °C. The structure of rhombohedral β-In_2Se_3 (0 0 9) was formed at 450 °C. The plane of β-In_2Se_3 (0 0 9) disappeared when the film was grown at 550 °C, instead a strong peak at $2\theta = 19.05^\circ$ defined as β-In_2Se_3 (0 0 6) and another weak peak at $2\theta = 48.35^\circ$ defined as β-In_2Se_3 (0 0 1 5) appeared. It is interesting to analyze why unstable β-In_2Se_3 phase could be found at room temperature without any intentional doping therein. It may be due to the doping effect of carbon given by the metal-organic precursor of TMI previously. The

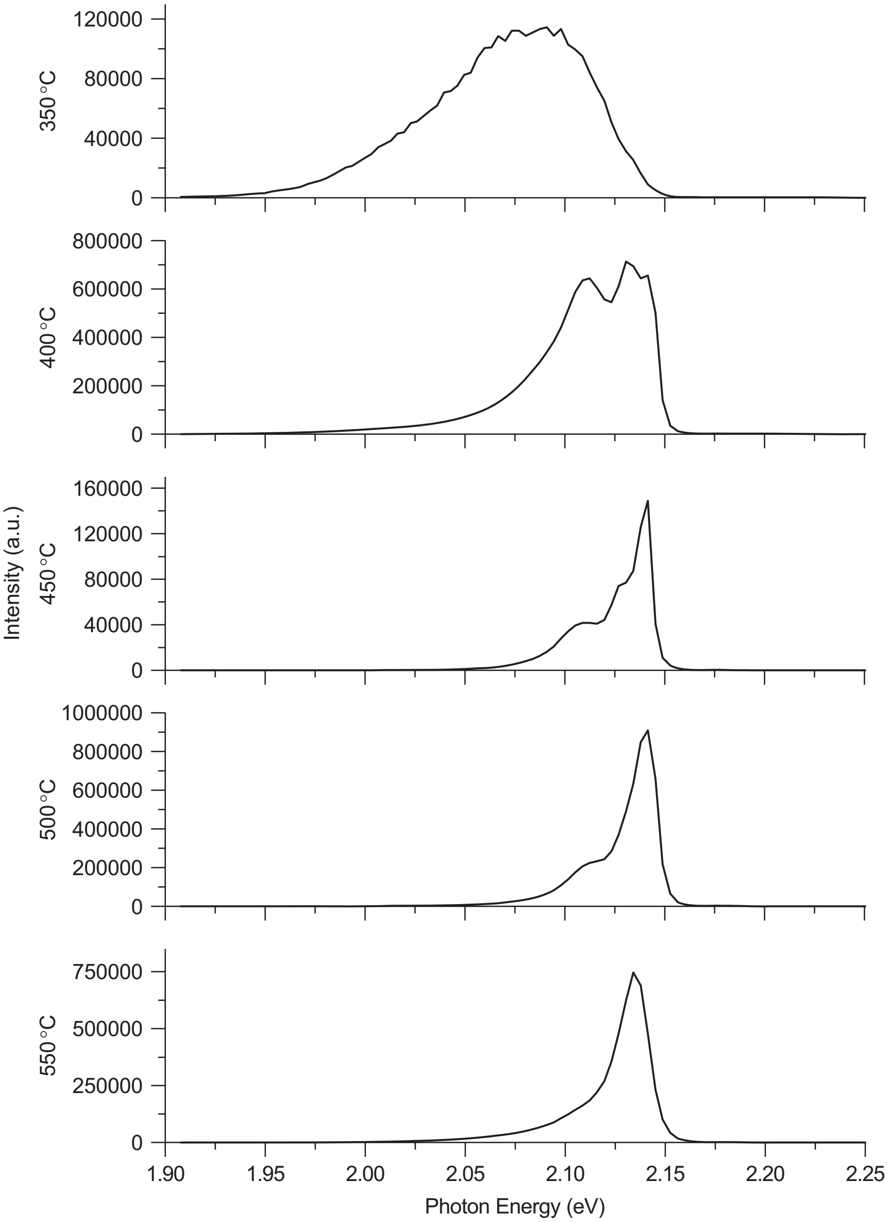

Fig. 3. 20-K PL spectra of In_2Se_3 films grown on the Si (1 1 1) substrates at 350, 400, 450, 500 and 550 °C, respectively.

doping effect of carbon may be the same as that of the Sb reported before [4]. Eventually, as the film was grown at over 450 °C, a more complicated structure was presented. In addition to the γ-phase In_2Se_3, the β-phase one also grew along the *c*-axis.

The surface morphologies of In_2Se_3 films are displayed in Fig. 2, which was taken by an SEM operated with the electron energy of 10 keV to present a magnification of 30,000. Columnar structure can be clearly observed from Fig. 2(a) and (b) but is absent from other images in Fig. 2. Namely, when the film was grown below 450 °C, only γ-phase appeared. Conclusively, polycrystalline In_2Se_3 thin films have been grown as analyzed by the SEM images.

Fig. 3 shows 20 K PL spectra of In_2Se_3 thin films grown on the p^+-Si (1 1 1) substrates at different temperatures ranging from 350 to 550 °C. PL measurements were also performed on the samples fabricated at both 600 and 650 °C. However, no PL spectrum could be obtained from the sample fabricated at 650 °C and only a weak PL emission was observed for that fabricated at 600 °C. As can be seen from Fig. 3a, strong PL emission at 2.14 eV was achieved for the films grown at 550 °C. This peak was also observed for the films grown at 400–500 °C. Besides the peak at 2.14 eV, there are also two other bands peaking at 2.13 and 2.11 eV, respectively. However, all these peaks became non-evident when the film was grown at 350 °C. Furthermore, the peak of 2.14 eV is reported to result from free exciton [17], while the other two peaks at 2.13 and 2.11 eV are considered to be caused by bound excitons [18]. Temperature-dependent (20–300 K) PL measurements were also carried out for all samples. Fig. 4 shows the evolution of PL emission with temperature for In_2Se_3 film grown at

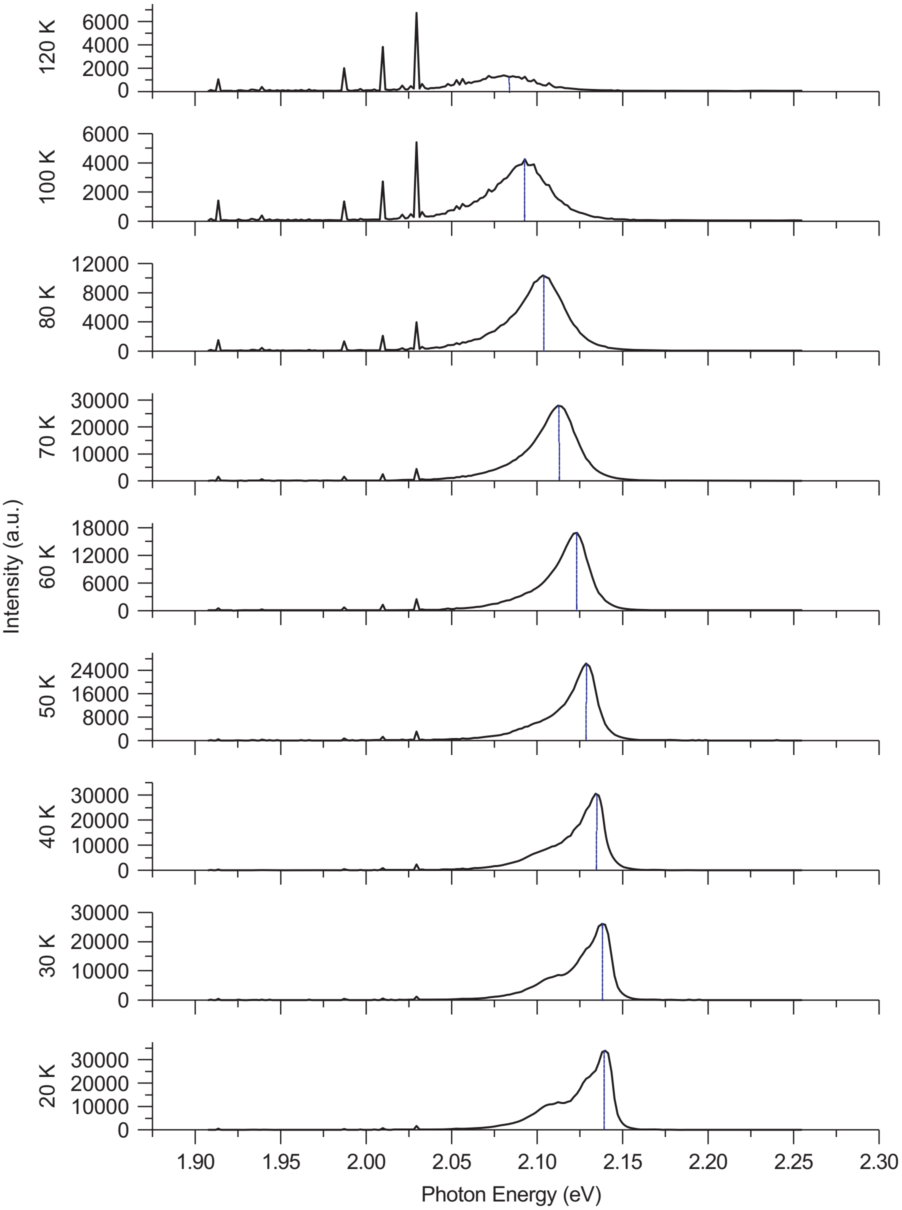

Fig. 4. Evolution of the PL emission with temperature for In_2Se_3 films grown on Si (1 1 1) at 450 °C.

450 °C, displaying clearly the intensity variation of free exciton and two bound excitons described previously. As can be seen, both bound excitons were activated finally and only free exciton was left. On the other hand, the free exciton dominated more evidently through the whole evolution of PL emission with temperature for In_2Se_3 film grown at 550 °C (not shown here). This is considered to be related to the material quality of films grown, such as more grain boundaries are presented by the film grown at a lower temperature. In addition, it was found that whatever the growth temperature of In_2Se_3 film was, thermal quenching behavior was evident in all PL spectra. The PL signal could only be recognized at a measurement temperature below 120 K. This is probably because once the measurement temperature is elevated more free excitons dissociate, and more carriers will be trapped by the defects and/or grain boundaries in the polycrystalline structure of In_2Se_3 film, which makes the PL intensity decrease. In addition, by examining the variation of PL peak energy as a function of measurement temperature and fitting to it the Varshni equation [19], the energy gap of the present material at room temperature was evaluated to be 1.95 eV. This value is well inside the range of 1.7–2.14 eV issued by other reports [20–22]. To further identify the excitonic nature, power-dependent studies were carried out. The power-dependent measurements at 20 K show that these peaks have different pump power dependencies. Fig. 5(a) and (b) shows the evolution of PL spectra with excitation power for In_2Se_3 films grown at 450 °C and 550 °C, respectively. As can be seen, the excitonic emission behavior is preserved for the film grown at 550 °C even a transition of dominance from free exciton to bound exciton occurs. However, for the film grown at 450 °C the PL spectrum redshifts and broadens quite obviously after the excitation power is over 30 mW and finally shifts outside the excitonic range, manifesting a luminescence with the involvement of impurities and/or defects. This result is another proof to support that good-quality In_2Se_3 film can be grown at the temperature of 550 °C.

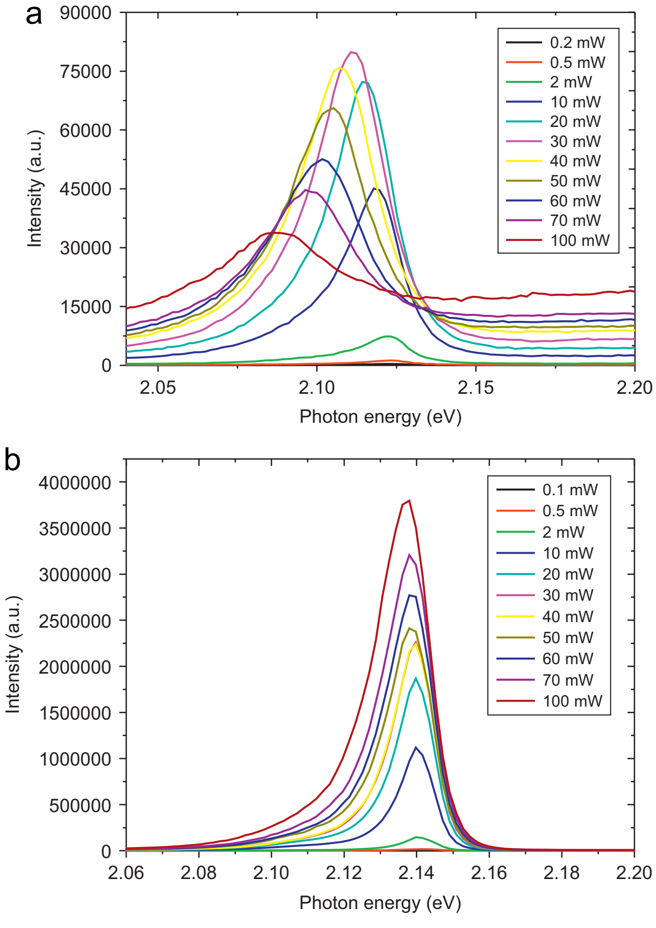

Fig. 5. Power-dependent PL spectra of In_2Se_3 films grown on the Si (1 1 1) substrates at (a) 450 °C and (b) 550 °C.

4. Conclusions

Polycrystalline In_2Se_3 films have been successfully grown on the Si (1 1 1) substrates by MOCVD at the temperatures higher than 500 °C. The XRD analyses demonstrate that the structure of In_2Se_3 films grown is greatly influenced by the growth temperature. Singular γ-In_2Se_3 was recognized when the grown temperature was below 450 °C, while β-In_2Se_3 could also be found when the film was grown at above 450 °C. PL measurements indicate the emission mechanisms to be free and bound excitons with the former being dominant for the films grown at higher temperatures. In addition, temperature dependent PL measurements help to resolve the energy bandgap of In_2Se_3 to be 1.96 eV. Finally, power-dependent PL measurements recognize the luminescent mechanism and the material quality of the films fabricated at 550 °C. It is concluded that the single-phase γ-In_2Se_3 films can be achieved at temperatures lower than 450 °C; however, good-quality In_2Se_3 films with the simultaneous appearance of γ- and β-phase structures can be grown at around 550 °C.

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