# Crystal phase control of indium selenide layers grown by molecular beam epitaxy

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## Introduction

Indium selenide attracts the research interest due to the high carrier mobility at room- and cryogenic temperatures. Indium selenide may exist in different crystalline phases including α-, β-, γ-InSe and $In_2Se_3$. Some of those allotropes belong to the family of van der Waals materials, in which two-dimensional layers are bound in the third dimension through weak van der Waals forces.

In this work we report the growth of indium selenide thin layers on (111)B-oriented GaAs and (111)-oriented $BaF_2$ substrates by molecular beam epitaxy under different growth conditions. Indium selenide thin layers were examined subsequently by using different techniques including photoluminescence (PL), atomic force microscope (AFM), X-ray diffraction (XRD).

## Experimental

Investigated samples were grown by molecular beam epitaxy (MBE). Substrates were first annealed in order to deoxydize the surface: (111)B-oriented GaAs at 600°C and (111)-oriented $BaF_2$ at 450°C. The growth temperature is varied in the range from 250°C to 475°C and In/Se flux ratio from 0.007 up to 0.33. The growth was monitored in situ by reflection of high energy electron diffraction (RHEED) which reveals streaky pattern corresponding to a flat surface in the entire range of the investigated parameters.

Optical properties were investigated by photoluminescence (PL) and micro-photoluminescence (μ-PL) in cryogenic temperatures and using 405nm excitation laser line .

## Conclusions

1) Indium selenide thin layers were successfully grown on (111)B-orientated GaAS and (111)-orientated $BaF_2$ substrates using molecular beam epitaxy.

2) Crystalline phase and properties of the samples strongly depend on growth temperatures and In/Se flux ratios, as shown on the phase diagram (Fig. 2).

3) High In/Se flux ratio leads to creation of wurtzite type γ-$In_2Se_3$ phase while lower In/Se flux ratio results in growth of characteristic crystalline structures, most probably corresponding with β-$In_2Se_3$ phase as well as mixed phases for intermediate flux ratio values. This is complemented by the AFM study which shows flat, triangular structures in case of low In/Se flux ratios, not present in samples grown using higher flux ratios.

4) Photoluminescence spectra shows additional emission peaks at lower In/Se flux ratio values below 2.12 eV, which experience blueshift with increased excitation energy. This could be interpreted as result of existence of type II heterojunction between mixed β- and γ-$In_2Se_3$ phases.

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## Results and discussion

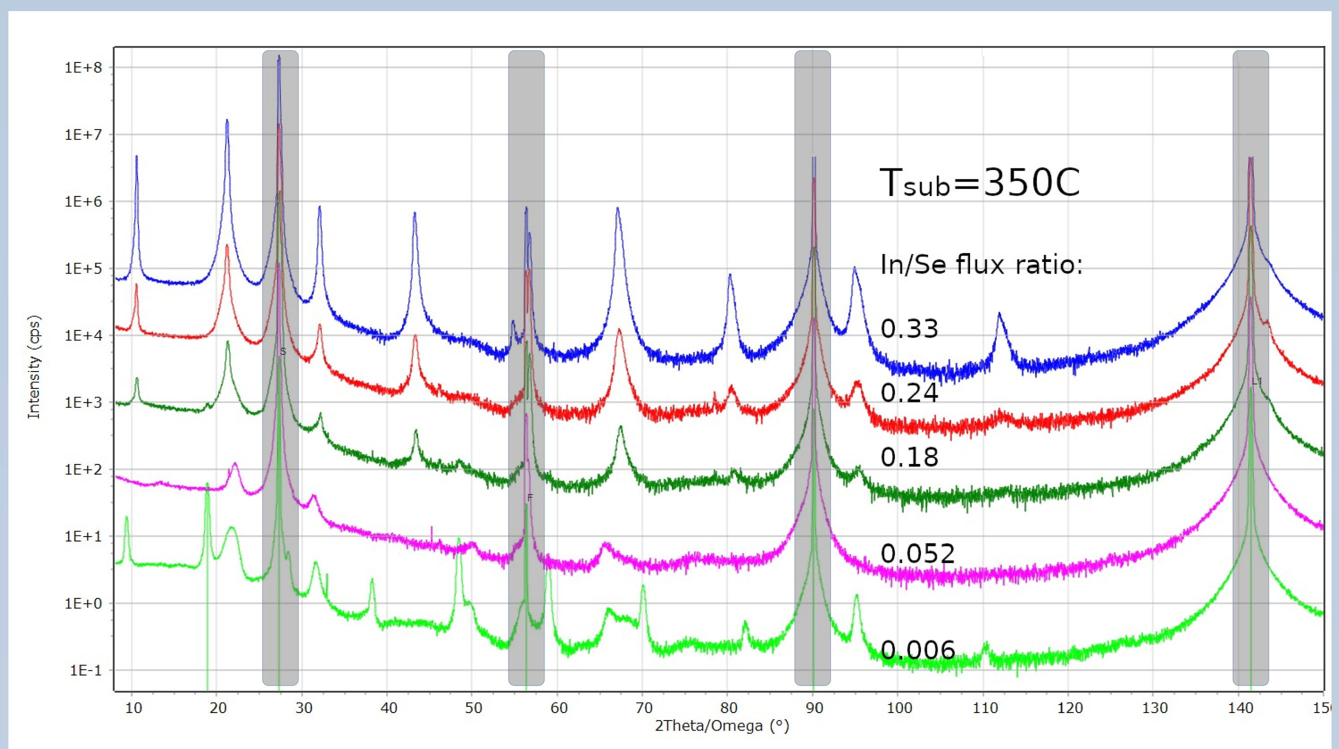


Fig. 1 X-ray diffraction from five different InSe thin layers grown on (111)B-GaAs substates at at $T_{subst}$=350°C with different In/Se flux ratio. These results confirm the existence of different indium selenide crystalline phases depending on the growth conditions. Grayed parts represent signal from GaAs substrate.

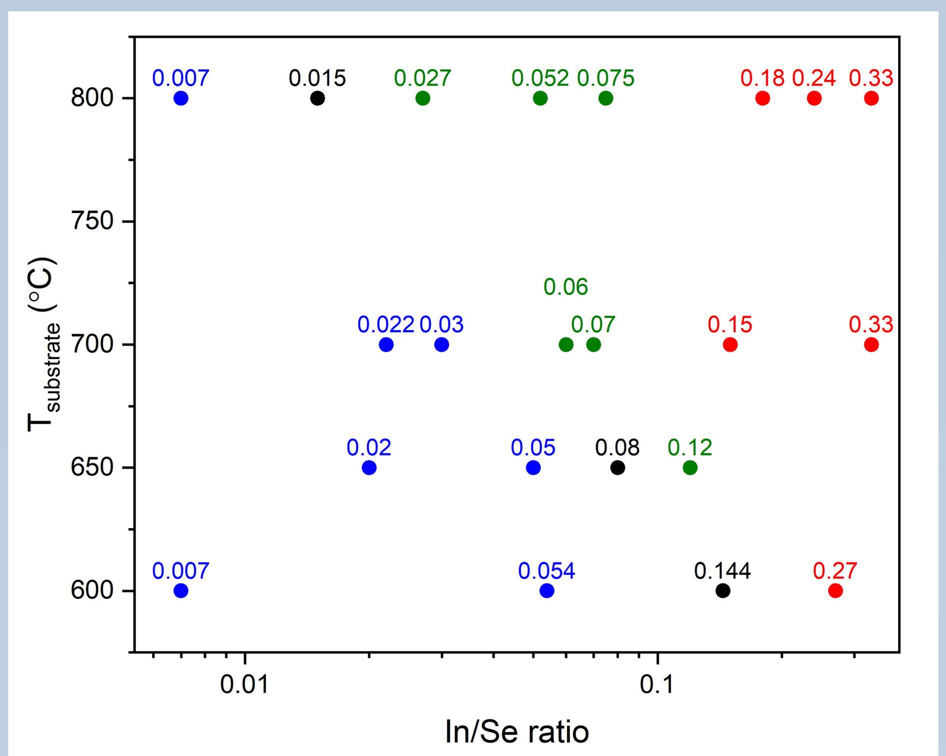


Fig. 2 Crystal phase diagram of indium selenide thin layers grown on (111)B-oriented GaAs substrate as a function of the growth temperature and In/Se flux ratio. Samples marked with blue color were interpreted as consisting of β-$In_2Se_3$ phase and red – of γ-$In_2Se_3$ phase with samples marked with green consisting of mixed β- and γ-$In_2Se_3$ phases.

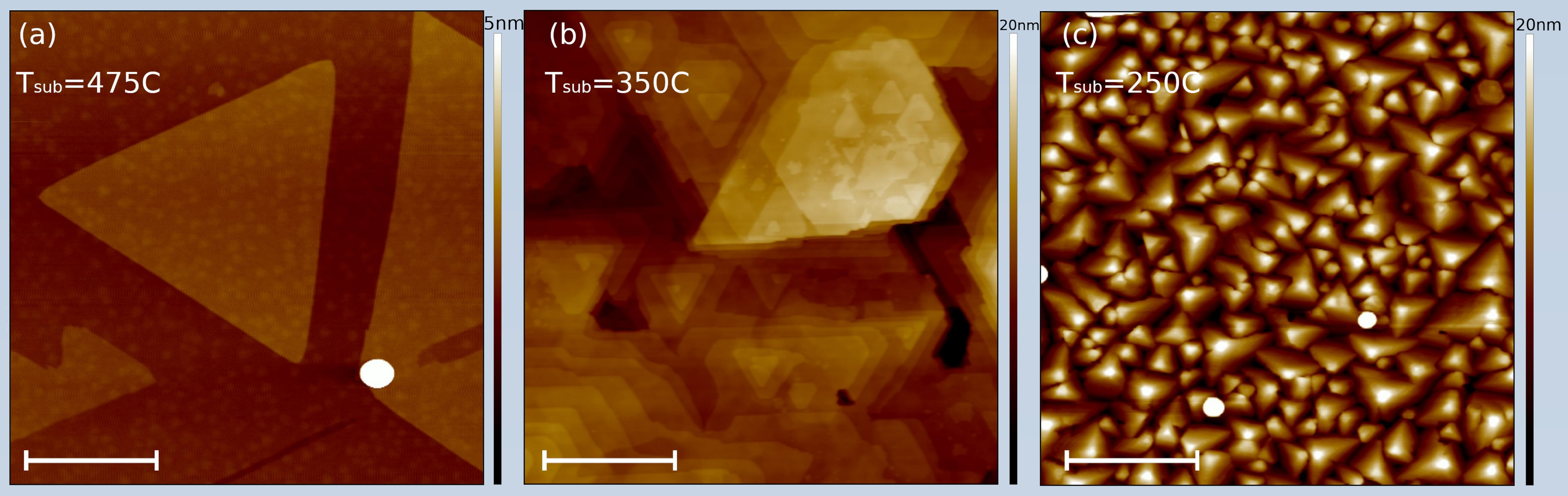


Fig. 3 Atomic force microscopy of indium selenide layers grown on (111)B-oriented GaAs at 0.007 In/Se flux ratio and growth temperatures: 475°C (a), 350°C (b) and 250°C (c) with height profile. Scale bar is 1μm.

AFM study reveals different structures on the surface depending on In/Se flux ratio and growth temperature. At In/Se flux equal to 0.007 and high (475°C) temperature, surface consist of triangular shaped structures with the side lengths of the order of 1 μm and the height of ~ 1.2 nm (Fig. 3 (a)). Decrease of growth temperature results in formation of crystalline structures consisting of significantly smaller triangular-shaped structures (Fig. 3 (b) and (c)). Similarly, increasing In/Se flux ratio within same growth temperature results in the presence more oblique structures with less sharp edges indicating a different indium selenide crystalline phase (Fig. 4).

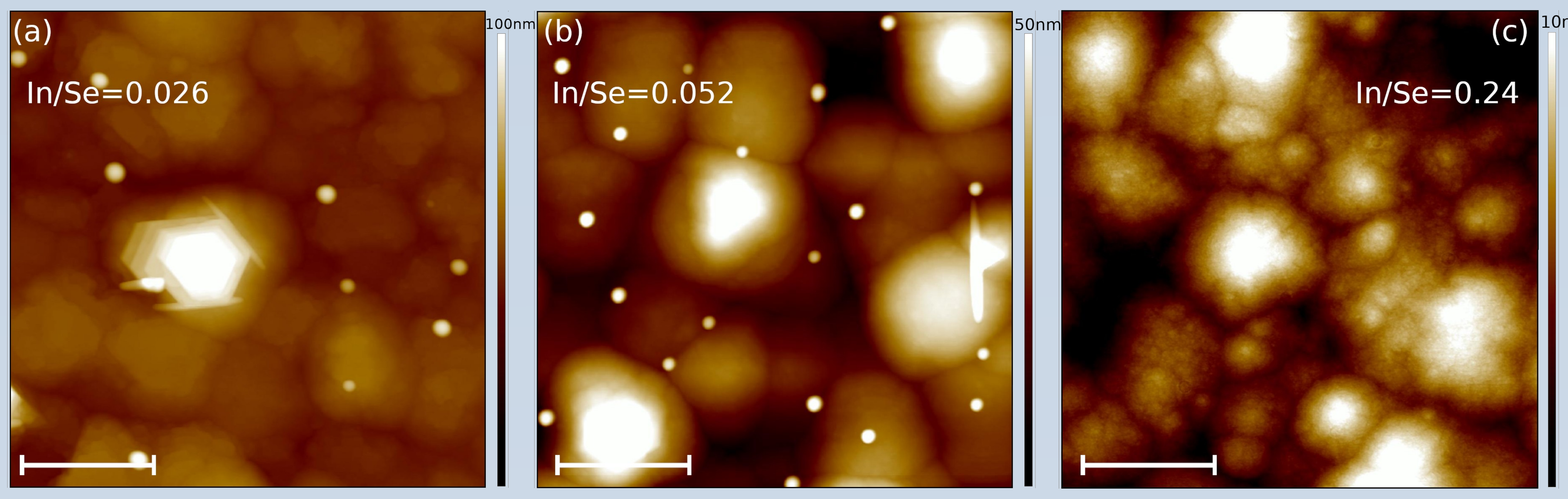


Fig. 4 Atomic force microscopy of indium selenide layers grown on (111)B-oriented GaAs at $T_{subst}$=350°C and 0.026 (a), 0.052 (b) and 0.24 (c) In/Se flux ratio with height profile. Scale bar is 1μm.

In the case of thin layers grown on (111)B-GaAs substrate and In/Se flux ratio above 0.24, the PL-spectrum consists of a single emission line at 2.15 eV which corresponds well to the bandgap of γ-$In_2Se_3$ (Fig. 5 (a)). When decreasing the In/Se flux ratio additional lines appear at 2.12 eV and 2.10 eV and become the most intensive emissions at In/Se equal to 0.05. These additional emission lines originate most likely from the inclusions of a different crystalline phase.

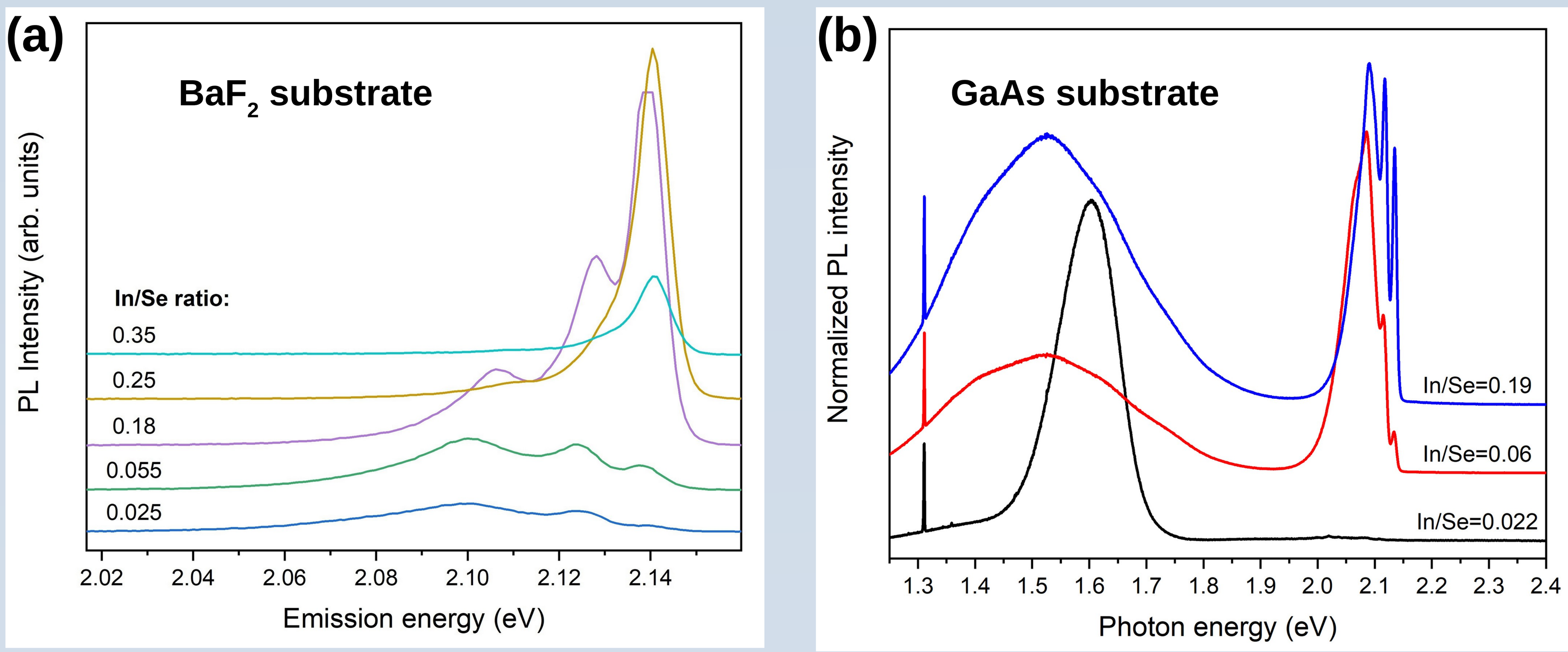


Fig.5 Photoluminescence spectra of indium selenide layers grown on: (a) (111)B-orientated GaAs substrate and (b) (111)-orientated BaF2 substrate. Growth temperature is 350°C.

PL-spectra of samples grown of (111)-$BaF_2$ (Fig. 5 (b)) shows emission lines at 2.15eV, 2.12eV and 2.0eV similar to the emission from the samples grown on GaAs substrates. The emission line at 1.6 eV typical for In/Se flux ratio below 0.022 corresponds to β-$In_2Se_3$ phase (Fig. 5). The emission lines appearing in the spectral range 2.12eV - 2.05eV show a dinstinct blueshift with increasing excitation power. Therefore, they are probably assigned to type II heterojunction between different InSe crystalline phases (Fig. 6).

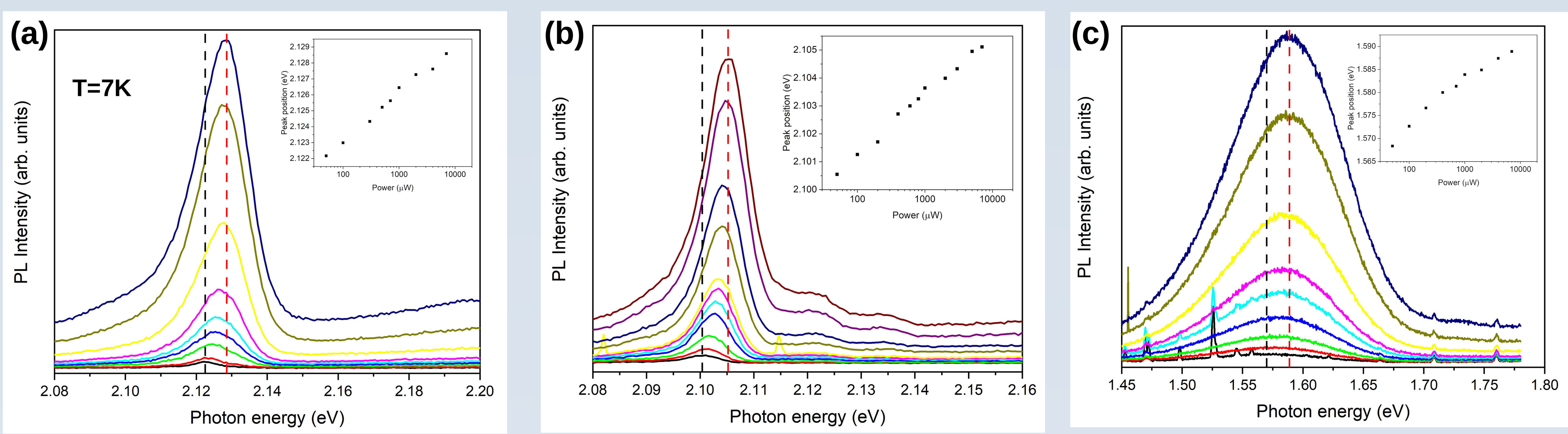


Fig. 6 Micro-PL spectra as a function of excitation power from indium selenide thin layers grown on (111)-orientated BaF2 substrate with In/Se flux ratio of 0.02 at 425°C (a) and 350°C ((b) and (c)). The emission lines in the spectral range 2.12eV - 2.05eV appear at random spatial positions.