

Optically active indium selenide crystal phase heterostructures grown by molecular beam epitaxy

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Indium selenide attracts the great interest due to its outstanding electronic and photonic properties, such as the excellent photo-responsivity, good electron mobility, robust room temperature ferroelectricity, high Seebeck coefficient and the large band gap tunability depending on the thickness. One of the challenges of fabrication indium selenide is the complexity of its phase diagram. Most of indium selenide crystalline phases belong to the family of two-dimensional (2D) semiconductors which are characterized by strong in-plane covalent bonds and weak interlayer van der Waals forces. Different crystalline phases of indium selenide may be characterized by a significantly different value of the band gap, e.g., the band gap of bulk γ -In₂Se₃ amounts to 2.15 eV and that of bulk γ -InSe to 1.32 eV (at cryogenic temperatures).

In this work we report on the crystal phase control of indium selenide thin layers during a molecular beam epitaxy (MBE) process. It is achieved by changing the growth conditions, such as the growth temperature and the indium to selenium flux ratio, during the growth. In the case of thin layers grown at 350°C on (111)B-GaAs substrate keeping indium to selenium flux ratio of 0.20 an almost perfect γ -In₂Se₃ crystal phase is obtained. This is confirmed by a comprehensive study involving X-ray diffraction and low temperatures photoluminescence which reveals a single emission line at 2.15 eV corresponding well to the bandgap of γ -In₂Se₃. In the next step, the MBE growth is stopped and the indium to selenium flux ratio risen up to 0.5. After the restart of the growth, indium selenide changes its crystal phase which is monitored *in situ* by a distinct change in the reflection of high energy electron diffraction (RHEED) pattern. This observation is consistent with atomic force microscopy study which reveals a remarkable change of the surface morphology: triangular shaped structures with the side lengths of the order of a few μ m and the height of \sim 1.2 nm are characteristic for the growth with the indium to selenium flux ratio of 0.5, while rather oblique structures without any sharp edges - for indium selenide growth with indium to selenium flux ratio of 0.2.

Interestingly, a quite intense optical emission in the near infrared spectral range appears as effect of the growth of the above described indium selenide crystal phase heterostructures. Moreover, it is found that the emission energy exhibits a distinct change depending on the average thickness of the second layer, from 1.1 eV for layers thicker than 20 nm up to 1.2 eV for a layer with the average thickness of 5 nm. This variation is consistent with the quantum size effect influence on the emission energy of thin layers. Furthermore, the photoluminescence lines exhibit a distinct blue shift with increasing excitation fluence. Based on the latter effect the observed optical emission is ascribed to the recombination at the type II interface between the two crystalline phases. Consistent with this interpretation is also the fact that the energy of this transition is lower than both: the bandgap of γ -InSe and the bandgap of γ -In₂Se₃. Inhomogeneity of indium selenide thin layers is investigated by spatially resolved cathodoluminescence revealing changes of max.40 meV of the emission energy depending on the spatial position of the excitation spot.

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