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The growth and characterization of $GaInSe_2$ single crystals

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Abstract. $GaInSe_2$ single crystals have been grown and characterized by experimental techniques such as high-resolution transmission electron microscopy, x-ray diffraction, x-ray photoelectron spectroscopy and optical and electrical measurements. The samples were prepared in single-crystal form from a melt. The structural analysis indicates that $GaInSe_2$ has a hexagonal structure, and confirms the high quality of the produced single crystals. Quantitative information on electrical and optical properties of single-crystalline $GaInSe_2$ was obtained by investigating the resistivity and photoluminescence as a function of the temperature and excitation intensity.

1. Introduction

In recent years, a considerable amount of effort has been devoted to studying $A^{III}B^{VI}$ semiconducting compounds, in order to understand their peculiar physical properties. The nature of the chemical bonding in these compounds causes special features, such as layered and chain structures, which are important both from a fundamental and from a technological point of view. In particular, layered semiconductors are stimulating increasing interest due to their potential optoelectronic applications [1]: their quasi-two-dimensional structural anisotropy, as well as their peculiar optical and photoconductive properties, have attracted investigators to the effort to acquire a better insight into the physics of these compounds [2].

The $A^{III}B^{III}C_2^{VI}$ chalcogenide semiconductors belong among the $A^{III}B^{VI}$-type layered-structure semiconductors [3]. Although the ternary semiconducting chalcogenides have been investigated extensively in recent years [4], very few investigations have been performed on $GaInSe_2$. This material, just like other ternary semiconductor compounds, could have many possible applications, ranging from use in solar cells to nonlinear optical technologies. Furthermore, it could be easily intercalated with foreign ions, atoms and molecules, thus offering the realistic prerequisites for producing controllable superlattices based on it.

The present study is the first systematic investigation devoted to the preparation of $GaInSe_2$ single crystals and to their characterization by experimental techniques such as x-ray diffraction, high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED), x-ray photoelectron spectroscopy (XPS) and resistivity and photoluminescence (PL) measurements. The samples were prepared in single-crystal form by using a vertical Bridgman–Stockbarge method [5]. The analysis obtained by electron diffraction, HRTEM and SAED indicated that $GaInSe_2$ has a hexagonal structure, and confirmed the high quality of the single crystals. The chemical composition was investigated by XPS and microprobe analysis, indicating that the single crystals had excess Ga. Quantitative information on the electrical and optical properties of the $GaInSe_2$ single crystals was obtained by resistivity and PL measurements.

2. The growth of the crystals

$GaInSe_2$ single crystals were grown from a melt using the Bridgman–Stockbarge technique [5]. Double-walled silica glass ampoules with the external part evacuated were used to minimize convection effects. The ampoules were cleaned by using first a mixture of HF and distilled water (1:3 by volume) and then pure alcohol. After chemical cleaning had been performed, the evacuated tube was baked to 1000 °C for 12 h. After the baking, a carbon liner was deposited by pyrolysis of methane at 1000 °C and then the tube was cooled down and loaded with stoichiometrically weighted amounts of high-purity (six nine) elements: 8.0389 g gallium (23.474%), 8.9923 g indium (26.256%) and 17.2150 g selenium (50.268%).

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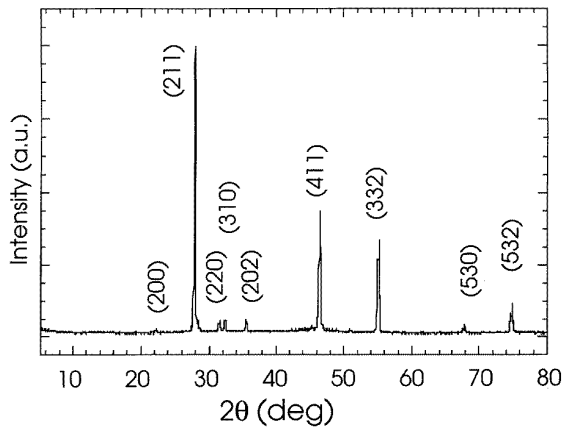


Figure 1. The x-ray diffraction intensity as a function of the Bragg angle of $GaInSe_2$ single-crystal powder.

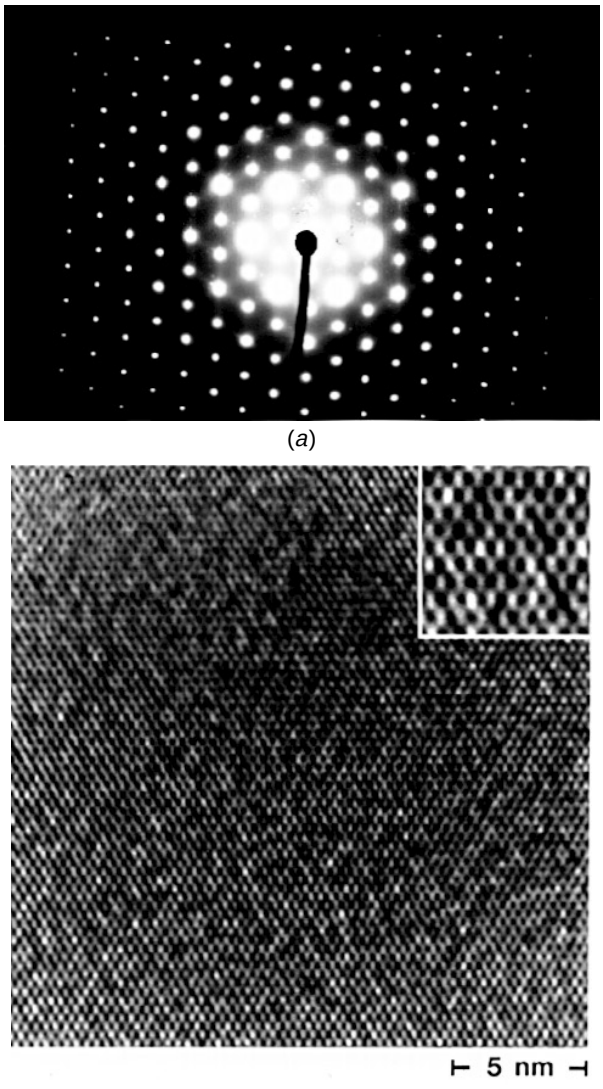
The ampoule was re-evacuated to a pressure of less than 10^{-6} Torr and sealed off. In order to avoid the formation of holes in the crystal, 100 Torr argon was added before the reaction crucible was sealed. Care was taken when heating the ingot to control the high Se vapour pressure and the exothermic reaction between Se and In. The mixture was slowly heated (0.5 °C min^{-1}) over a temperature range of 200–250 °C to minimize the risk of cracking the ampoule. The temperature was kept at 950 °C for 48 h to homogenize the melt. The crucible was then lowered from the hot side to the cold side at 350 °C at a speed of 0.458 mm h^{-1}.

3. The structural analysis of the crystals

After the product had cooled to room temperature, the crystal was identified by means of x-ray powder diffraction measurements as a single phase with lattice constants $a = 8.002$ Å and $c = 6.5372$ Å. These results are in good agreement with previous x-ray structure investigations for $GaInSe_2$, which indicated $a = 8.051$ Å and $c = 6.317$ Å [6]. In figure 1, the peaks of the x-ray powder diffractogram as a function of 2θ (twice the Bragg angle) are reported. The typical size of the monocrystals was of the order of a few millimetres.

In general, $A^{III}B^{III}C_2^{VI}$ chalcogenide semiconductors were at first believed to have a tetragonal structure [7]. Later investigations attributed the crystals to the monoclinic system instead [8–10], although polytypical modifications with the other crystal structures have also been reported [11]. In order to investigate the structure of the $GaInSe_2$ single crystals in detail, HRTEM and SAED studies were performed. For HRTEM and SAED studies, a Hitachi HF 2000 TEM equipped with a cold field-emission gun was used. A Cambridge S-100 SEM was employed to obtain backscattered electron images which reveal a chemical contrast between phases with different chemical compositions.

In figure 2, the [001] SAED pattern (figure 2(*a*)) and the corresponding HRTEM image (figure 2(*b*)) of $GaInSe_2$ are presented. The inset shows a detail with ×2 magnification. Our results clearly indicate that the crystal structure of our $GaInSe_2$ single crystals is hexagonal. Notice that the HRTEM image shows a weak variation in contrast, which could be due to the clustering of In and/or Ga in small islands.

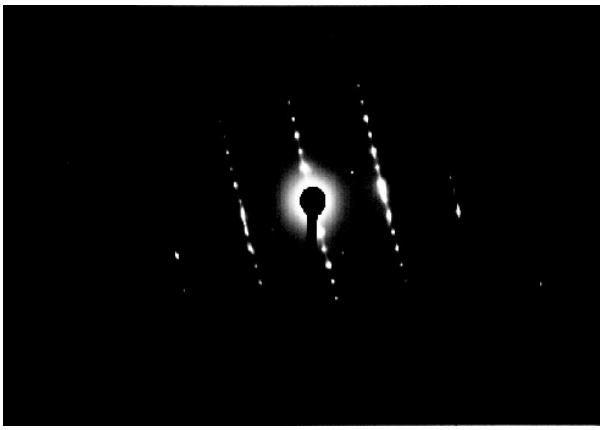


(*a*)

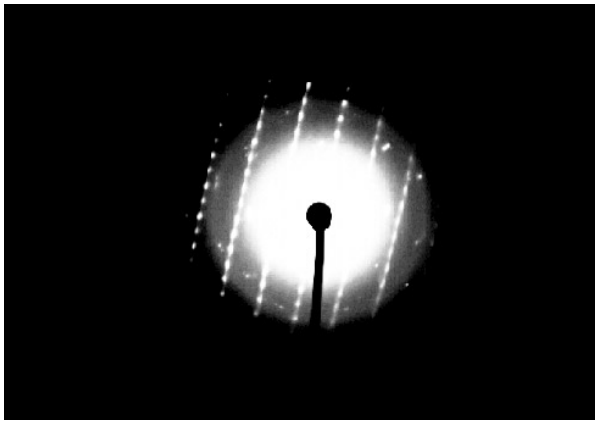
(*b*)

Figure 2. Selected-area electron diffraction along the [001] axis of a $GaInSe_2$ single crystal (*a*) and the corresponding high-resolution transmission electron micrograph (*b*). The inset shows a detail with ×2 magnification.

The SAED patterns obtained from the hexagonal $GaInSe_2$ at different orientations revealed the modulated structure of the $GaInSe_2$ phase and the fact that the crystal structure is incommensurably modulated along the hexagonal axis, as shown in figure 3. This result also agrees with a previous investigation [6], which reported $GaInSe_2$ to crystallize in one-dimensional linear chains of edge-sharing $GaSe_4$ tetrahedra parallel to the *c* axis of the tetragonal unit cell, with the indium–indium distances within the indium chains running parallel to *c* not commensurate with the tetrahedral chains. This gives rise to an incommensurate superstructure with a complicated pattern.



(*a*)



(*b*)

Figure 3. Selected-area electron diffraction at orientation [100] (*a*) and [210] (*b*) along the hexagonal axis of the $GaInSe_2$ single crystal.

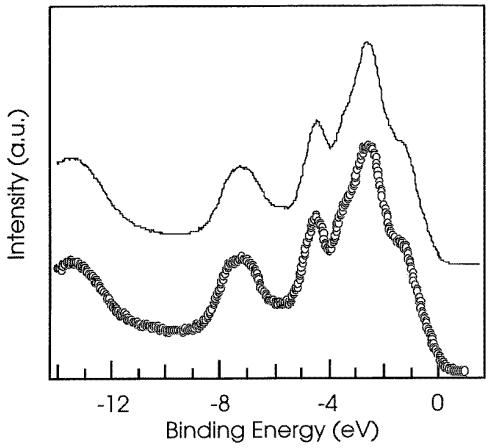


Figure 4. Valence band x-ray photoemission spectra of GaSe (circles) and $GaInSe_2$ (full line) single crystals.

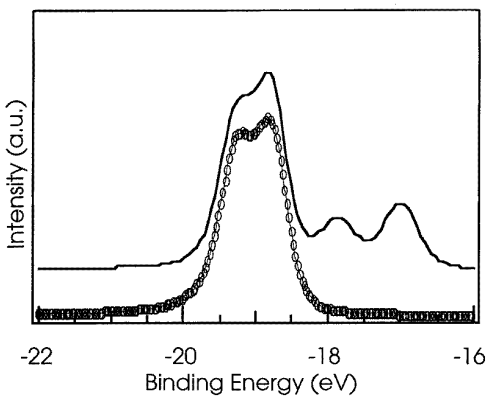


Figure 5. Ga 3d and In 4d doublets of GaSe (circles) and $GaInSe_2$ (full line) single crystals.

4. The chemical characterization of the crystals

XPS is very effective in the study of the valence-band structure and of the core levels of different atoms. From XPS data, we obtained information on the electronic structure, the chemical composition, the chemical status of each element and other parameters. The XPS measurement were performed by using a Scienta ESCA 300, described in detail in [12]. The operating pressure was better than 3×10^{-10} mbar, with an energy resolution of 0.3 eV. The monochromatized x-ray beam was the Kα emission line of aluminium (1486 eV) produced by a 3 kW rotating anode. Electrons ejected by such photons from the valence bands have typical escape depths of 20 Å, corresponding to several lattice constants, and therefore results typical of the bulk are to be expected. The core-electron binding energies are reported and all values were corrected for the spectrometer's work function and sample charge build-up by using the gold $4f_{7/2}$ level peak as a calibration reference. The core-level energies are given with respect to the Fermi level. The samples were analysed *in situ* by scanning the regions around the oxygen and carbon 1s peaks: no oxygen or carbon could be detected.

In figure 4 the valence-band XPS spectra of GaSe and $InGaSe_2$ are compared. The features observed in the case of GaSe are in good agreement with the theoretical band-gap calculations [13]. Although no band-gap calculation has been published for $GaInSe_2$, the comparison of its spectra with those of GaSe is quite instructive: the Ga–In substitution has an almost negligible effect on the valence band.

Figure 5 show the Ga 3d and In 4d spectra. Each element produces a spin–orbit doublet. The In 4d doublet (16.80 and 17.69 eV) is quite close to the Ga 3d doublet (18.65 and 19.20 eV). Note that the integrated Ga 3d intensity is larger than the integrated In 4d intensity. By taking into account the cross section values we found that the Ga concentration is slightly larger than the In concentration. This information is in agreement with results from microprobe analysis, thus indicating that there is an In deficiency at the cleavage surface.

5. The electrical analysis of the crystals

In order to perform electrical and optical analyses, samples were cut from a large ingot (2.2 mm × 1.0 mm × 1.0 mm) by using a low-speed diamond cutter. A rotating-disc polishing process was necessary in order to obtain a bulk specimen with an optically flat and parallel surface. A mixture

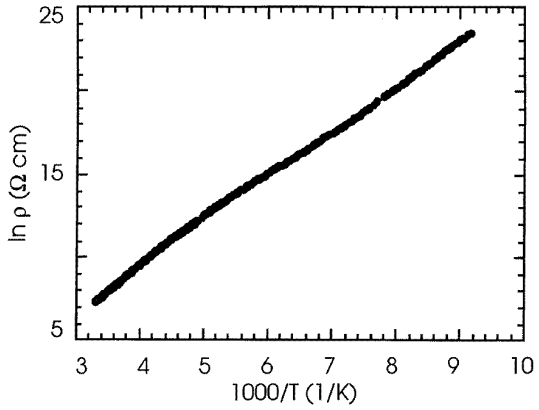


Figure 6. Semi-logarithmic plot of the temperature dependence of the DC electrical resistivity of $GaInSe_2$ single crystals.

of 1.0 mm α-alumina and 0.005 mm β-alumina was used during the fine polishing process. After the specimen had been polished, it was washed with pure ethyl alcohol, then with hot twice-distilled water and allowed to dry without any heat treatment. Precise determination of the specimen dimensions, which is needed for the precise calculation of electrical properties, was carried out with an optical microscope.

By using a thermoelectric-power probe we found that our samples exhibited p-type conductivity. The temperature dependence of the DC electrical resistivity has been measured in the range 4.2–300 K. The sample was contacted in a four-point probe configuration in order to eliminate contact resistance. The gold wire electrodes (50 μm in diameter) were attached to the sample by using ultrasonically soldered indium contacts in order to minimize the contact resistance. A helium glass cryostat in which the temperature could be stabilized to within 0.1 K was used. The temperature was monitored by using a carbon glass resistor. A computer-controlled data-acquisition system was used.

A semi-logarithmic plot of the temperature dependence of the DC electrical resistivity of $GaInSe_2$ single crystals in the range 4.2–300 K is shown in figure 6. These results indicate that there is an exponential behaviour according to the relation $\exp[-E/(kT)]$, k being the Boltzmann constant and E the activation energy. A thermal activation energy of the majority carriers (holes) of 51.95 meV was obtained by fitting the results in figure 6. A resistivity of $\rho = 1.58 \times 10^3$ Ω cm was observed at room temperature.

6. The optical analysis of the crystals

The dependence of the PL spectra on the temperature and excitation intensity was investigated using a He closed-cycle cryostat, whose temperature could be varied in the range 8–300 K accurately to within ± 0.5 K. The samples were photoexcited by using the 514 nm line of an Ar-ion laser, whose light beam was focused onto a spot of about 100 μm diameter, and the signal was detected by a cooled GaAs photomultiplier and recorded using photon-counting techniques. The typical laser excitation intensity was about 10 W cm^{-2}. An energy gap of $E_g = 1.77$ eV was

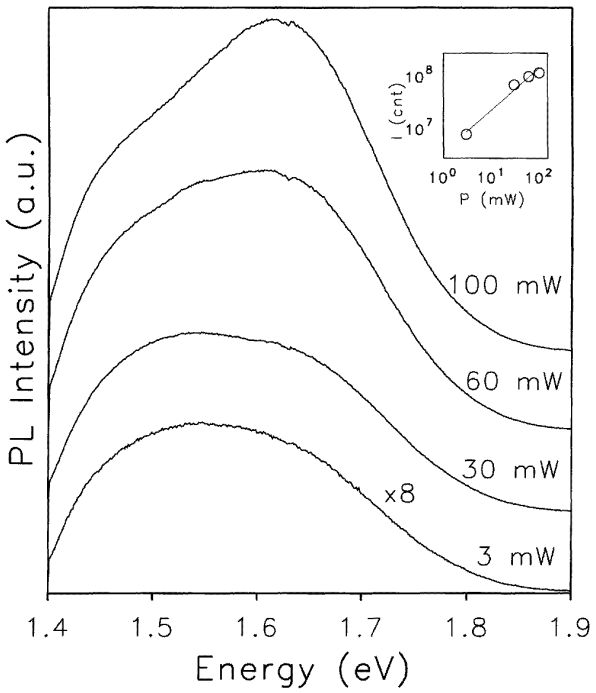


Figure 7. Photoluminescence spectra as a function of the excitation intensity P. The dependence of the total PL intensity on P is shown in the inset.

evaluated by means of low-temperature (12 K) reflectance measurements, the energy gap of $GaInSe_2$ as expected being slightly higher with respect to that of $GaInTe_2$ (1.62 eV) because of the substitution of Te by Se.

In figure 7, PL spectra at various excitation-intensity levels are reported. The PL spectra show two broad bands at about 1.62 and 1.44 eV. As the excitation intensity is increased, the low-energy band is observed to saturate, as expected in the case of radiative transitions due to impurity-bound states. The dependence of the total PL intensity on the excitation intensity is reported in the inset of figure 7. A power-law dependence with a critical exponent of 0.80 was observed, indicating the dominant role of extrinsic recombination in the PL spectra of our samples.

In figure 8, the temperature dependence of the PL spectra at low excitation intensity (10 W cm^{-2}) is reported. Because of the low excitation, only the low-energy bound states are present. As the temperature was increased, the recombination was observed to shift to lower energies (because the gap shrank), and the overall PL intensity was observed to decrease (because of non-radiative recombination). Figure 8(a) is a semi-logarithmic plot of the PL intensity as a function of the reciprocal temperature. In the limit of high temperature, for which thermal equilibrium can be assumed, an Arrhénius law-type behaviour was observed, in good agreement with the activation energy derived from the resistivity measurements (full line). Thus, the localized states involved in the electrical conductivity seems to be the same centres which are responsible for the extrinsic luminescence. Figure 8(b) shows the red shift ΔE of the PL line as a function of the temperature. The band-gap reduction can be described by

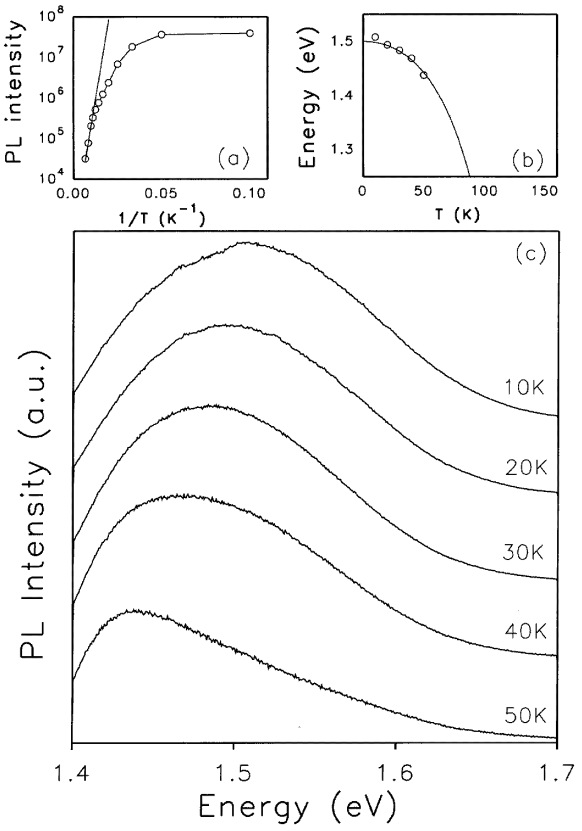


Figure 8. Photoluminescence spectra as a function of the temperature (*c*). The dependences of the total PL intensity (*a*) and of the recombination energy (*c*) on T are also shown.

the Varshni relationship [14], $\Delta E = -\alpha T^2/(\beta + T)$, where α and β are material-dependent parameters. α represents the linear shift of the energy gap at high T, whereas β accounts for the quadratic trend at low T. By fitting our experimental results to the Varshni equation, we obtained $\alpha = 30 \times 10^{-4}$ eV K^{-1} and $\beta = 180$ K, comparable with the results obtained for other III–VI compounds [15].

7. Conclusions

We investigated the properties of $GaInSe_2$ single crystals produced in our laboratory, demonstrating their high quality. We determined several important physical properties of this compound, such as the structure, the hole activation, the band gap and the Varshni parameters. Such data provide the necessary background for additional investigations on this promising semiconductor material.

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