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II-VI Semiconductor microstructures: from physics to optoelectronics

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Abstract. — The tellurium compounds family displays many interesting features. The various compounds cover a very large range of bandgap energies from 0 (Cd$_{0.15}$Hg$_{0.85}$Te) to more than 3 eV (ZnTe: 2.4 eV; MnTe: 3.2 eV; MgTe: 3.5 eV). The lattice parameters of the various compounds are sometimes almost perfectly matched, as in the CdTe/Cd$_{1-x}$Hg$_x$Te case, or slightly enough mismatched for a coherent epitaxy to be performed. Furthermore, good quality Cd$_{0.99}$Zn$_{0.04}$Te substrates are now available which allow to grow a large variety of microstructures using molecular beam epitaxy. The thickness control of the deposited layers allows to design and grow sophisticated heterostructures incorporating monolayer thick features. The direct band gap of these materials makes them well-suited to many optoelectronic applications in the infrared and visible range. A few examples of applications are described in more details: i) microtip semiconductor laser based on a cold microtip electron emitter for cathodic pumping of a CdTe/CdMnTe laser cavity; ii) multiquantum well structures showing a marked excitonic absorption band at room temperature and the disappearance of this band when an electric field is applied to the structure. Application to self electrooptic and photorefractive devices; iii) Bragg mirrors for the infrared. In addition to the usual semiconductor properties, the manganese compounds display interesting properties which can be useful in the field of magnetooptics.

Introduction.

The optoelectronic applications of semiconductors devices are closely linked to the fundamental properties of the semiconductors from which they are made. The development of new materials will then open new functional possibilities. This will certainly also be the case for II-VI semiconductors whose technology is in rapid progress.

The II-VI semiconducting materials cover a large range of bandgap energies from 0 (some of these compounds are semimetals like HgTe and HgSe) to more than 4 eV. In addition they all have a direct bandgap suited to light emission or absorption. This is the reason why these materials have been used for many years as luminophors. However their development has been slowed in the past by the poor quality of the crystals and the difficulty in controlling the doping. These points are now much better controlled thanks to the development of bulk or thin...
layer crystal growth techniques. Among these is the Molecular Beam Epitaxy technique which offers high quality and versatility for the preparation of micron thick layers.

We will first introduce to the general properties of II-VI materials and describe some sophisticated heterostructures to give the reader an idea of the state of the art in the MBE growth of these materials (Sect. 1). Next we will describe the different ways which are presently explored for the fabrication of solid state lasers emitting in the blue green region of the visible spectrum (Sect. 2). New applications in the near infrared come from the « band gap engineering » capability of the complex heterostructures: modulators, photorefractives (Sect. 3). The mid infrared (3 to 5 μ) and the far infrared (8 to 12 μ or more) have always been specific domains of these materials. New possibilities of infrared lasers are opened with the help of the new preparation techniques (Sect 4).

1. Tellurium-based II-VI semiconductors.

1.1 General properties. — In the following we will mainly restrict ourself to the tellerium-based compounds. The experimental results which will be presented have been obtained on the structures prepared and studied, at Grenoble, by the CEA-CNRS group « Microstructures de Semiconducteurs II-VI ». The selenium-based compounds constitute another important class of the II-VI family, whose study is in huge development throughout the world for visible laser applications. They will be briefly described in the next section.

In figure 1, the tellerium compounds are presented by their bandgap vs. lattice parameter. The right hand scale indicates the wavelength of the photon absorbed or emitted at the bandgap energy. Cd₁₋ₓMnₓTe and CdₓHg₁₋ₓTe alloys are able to emit light at any wavelength in the visible spectrum while CdₓHg₁₋ₓTe compounds cover the infrared range until very large wavelengths [1]. A very interesting feature of the CdₓHg₁₋ₓTe compounds comes from the constant lattice parameter of the various compounds. They all can be grown epitaxially on a CdTe substrate without any serious lattice mismatch.

The direct band gap of these compounds make them suited to the various photonic interaction processes. In addition the electron effective mass, which governs the absorption probability, is larger than in III-V compounds of similar band gap. For example in CdTe m* = 0.12 m₀, to be compared to 0.064 m₀ in GaAs. The result is a smaller excitonic Bohr radius, with larger excitonic binding energies. The oscillator strength is then 2 to 4 times larger in II-VI semiconductors. Some specific applications of that will be described in section 3.

The large changes of the refractive index associated with the composition variations will be used for the light confinement in laser structures or light guides. Lastly the very large values of the electrooptic coefficient and of the associated figures of merit will be used in photorefractive devices described later.

1.2 Growth of II-VI microstructures. — The crystal growth techniques which have recently been developed, such as molecular beam epitaxy, allow the epitaxial regrowth, on a convenient substrate, of layers of high crystalline quality. Composition and thickness may be adjusted to a predefined value. However if a close lattice match between the various layers is not realized, many structural defects of detrimental effect will appear.

1.2.1 Substrates. — For this reason the substrates must be matched as closely as possible to the layer to be grown. They must also be isovalent (e.g. II-VI substrates for II-VI layers, etc.) in order to reduce the parasitic doping of the layer by the substrate (III and V elements are efficient dopants of II-VI semiconductors). A supplementary advantage would be to have a substrate which is transparent to the wavelength to be used. These various conditions are frequently fulfilled by the Cd₁₋ₓZn₁Te substrates which are commercially available with
$4 \leq x \leq 20\%$. The substrate size reaches now 25 cm$^2$ (for $x \equiv 4\%$). The representative points of these substrates are indicated in figure 1. They are lattice matched with a large range of Cd$_{1-y}$,Mn$_y$Te and with all the Cd$_{1-y}$,Mg$_y$Te or Cd$_{1-y}$,Hg$_y$Te compounds. Their wide bandgap makes them transparent to any wavelength larger than 750 nm.

1.2.2 Thickness and composition control. — The crystalline quality and the grown thickness are in situ controlled by reflection high energy electron diffraction (RHEED) under grazing incidence. This technique detects the periodic decrease of the surface roughness, which occurs each time that a molecular layer has been completed on the flat surface. The monolayer control of the deposited thickness is then possible, allowing so a high accuracy to be reached in the definition of the quantum structures and of their electronic properties. An illustration of the possibilities opened by the thickness control down to the monolayer is given in figure 2. This is the transmission electron microscopy of CdTe samples in which several planes made of 1, 2 or 3 monolayers of ZnTe have been inserted [2]. The precision of the thickness control may be estimated to be better than 0.15 monolayer. By the alternate deposition of CdTe and ZnTe layers this technique might be used to produce artificial pseudo alloys ordered in one direction. The composition of the alloys is determined, during the growth, by measuring the growth rates. The reproducibility may be better than 1%.

1.2.3 Interdiffusion. — Once the growth is achieved, it may be interesting to check to which extent the interdiffusion has smoothened the interfaces. This point has been studied in great
Fig. 2. — Barriers of ZnTe of thickness (a) 1, (b) 2, (c) 3 monolayers inserted in CdTe. The pictures are Transmission Electron Microscopy cross sections. Picture (d) is the high resolution analysis of picture (b).
detail, thanks to X-ray diffraction by superlattices [3]. It could be established that the interdiffusion does not concern more than 1 monolayer for CdTe/ZnTe at a temperature lower than 320 °C and for Cd_{0.5}Hg_{0.5}Te/CdTe under 180 °C. For HgTe/CdTe the temperature conditions are more stringent (less than 160 °C) if the interdiffusion has to be limited to 2 monolayers.

1.2.4 Doping. — The full use of the possibilities of a semiconductor requires the doping n or p type. The materials whose MBE growth is well-controlled, are now routinely doped. For ZnSe the doping is performed with chlorine (n-type) or atomic nitrogen (p-type). For CdTe the donor impurity is indium, while the acceptor dopant is arsenic. Doping with atomic nitrogen is in progress. Cd_{1-x}Hg_xTe is doped n-type with indium.

2. Optical functions in the visible range.

2.1 VISIBLE SOLID STATE LASERS WITH Se-BASE COMPOUNDS. — In 1991, several American teams have demonstrated that p-type doping of ZnSe was possible with atomic nitrogen as a dopant and that a blue green injection laser could be made [4]. Devices of this type, emitting around 510 nm until the room temperature have been realized. The emission threshold is lower than 2.5 mA. The best material combination is found in ZnMgSSe alloys deposited on a GaAs substrate and lattice matched to it [5, 6]. The main problem of these devices is their very short lifetime which is less than 1s for cw emission at room temperature. There are still serious progress to be done in the material and device quality control.

2.2 VISIBLE SOLID STATE LASERS WITH Te-BASED COMPOUNDS. — As indicated above these compounds may be prepared lattice matched to an isovalent CdZnTe substrate. Parasitic strains and contamination are then minimized. Taking the figure 1 as a reference, it can be observed that manganese, as well as magnesium compounds, can be used to cover the visible range. The first ones have been studied for a few years. Light guiding structures with graded index have been grown and excited with optical or electronic pumping. The figure 3 is the secondary ions mass spectroscopy (SIMS) analysis of the manganese content of a graded index separate confinement heterostructure (GRINSCH). The bandgap variation is directly linked to the manganese concentration. The two lateral gradients collect the carriers in the central

![SIMS : Mn](image)

**Fig. 3.** — Secondary Ions Mass Spectroscopy (SIMS) of the manganese content of a GRINSCH CdTe/CdMnTe structure containing two 5 nm quantum wells.
quantum wells where they recombine. The recombination light is guided in the central region by the index gradient associated with the composition variations. Optical gain has been measured on these structures. It reaches 200 cm\(^{-1}\) at 95 K and 20-30 cm\(^{-1}\) at 300 K. Laser emission is then possible with 300-500 \(\mu\)m long structures [7, 8]. The figure 4 displays the emitted intensity \(vs.\) the pumping power at 95 K. The inset shows the emitted spectrum with the characteristic cavity modes. The central wavelength of 763 nm is still on the edge of the visible spectrum. Devices emitting at shorter wavelength, at least in the green-yellow range, are in development.

![Figure 4](image)

Fig. 4. — Laser emission \(vs.\) the pumping power for a microgun pumped CdTe/CdMnTe heterostructure. Inset shows the emission spectrum dominated by the Fabry-Pérot modes.

2.3 MICROGUN PUMPED SEMICONDUCTOR LASERS. — The results of figure 4 have been used to demonstrated the feasibility of a new device the « microgun semiconductor laser » based on a cold low voltage electron source [7, 9]. This source is illustrated in figure 5. It is a device specifically developed starting from the flat display screen technology used by LETI at Grenoble. A large number of microtips (about \(10^4\) \(cm^{-2}\)) are deposited on a conducting substrate. Correctly biased (100 V) they emit electrons which are accelerated with a 10 kV voltage and focussed on the semiconducting target. The target is a semiconductor heterostructure whose bandgap reproduces the composition profile of figure 3 : the active region is made of 1 or more quantum wells sandwiched between 2 gradients regions. Each electron impinging on the semiconductor creates several thousands of electron-hole pairs whose radiative recombination generates light.

The device is schematically shown in figure 5a as well as the cross section of a single tip (b). The semiconducting target used up to now is a CdTe/CdMnTe structure, described in the previous paragraph. The development of a CdMgTe structure is in progress. It could also be possible to use a ZnMgSSe structure similar to the one used in the blue-green injection lasers.
Better lifetime performance can be expected since the microgun semiconductor laser technology does not require any good ohmic contact to the semiconductor device. The microgun semiconductor laser may appear in the near future, as a useful new device concept.

3. Optical devices for the near infrared.

3.1 Optical Modulators. — We have already pointed out that II-VI quantum structures are efficient to absorb light, at a wavelength which is specific of each quantum structure. Furthermore, we are going to show that this absorption may be easily modulated by the application of an electric field. The basic phenomenon, known as Stark effect, arises from spatial separation of electron and hole, in the quantum well, under the action of the electric field. The result is a lowering of the photon energy (red shift) needed for the creation of an
electron-hole pair. The transition probability is also reduced because of the smaller overlap of the electron and hole wave-functions.

The band structure of a quantum well without and with electric field is schematized in figures 6a and b. In a practical device the electric field may be the space charge field of a Schottky diode. Figure 6c shows the absorption spectrum of such a device containing five 12 nm CdTe quantum wells separated by 20 nm Cd$_{0.8}$Zn$_{0.2}$Te barriers under various biases. The maximum optical density is obtained for a 0.7 V direct bias (zero electric field). The absorption almost disappears under an electric field of 2 x 10$^4$ V/cm [10]. This non linear behavior may be used to make a light modulator of the self electrooptic device (SEED) type. It is obtained if the Schottky device is biased across a load resistance. The $I(V)$ characteristic of the illuminated device shows a pronounced hysteretic behavior due to the current induced counterreaction. The transmitted light displays a similar behavior. A typical non linearity is reproduced in figure 7: at constant bias (−0.5 V) the transmitted power decreases abruptly above a threshold power. The threshold is different on increasing and decreasing powers. This curve, as well as the spectra of figure 6 have been recorded at low temperatures but similar results are now obtained at room temperature [11, 12]. The optical modulation possibility has been demonstrated at 0.8 μ and also around 0.5 μ [13]. This could be extended to other wavelengths by properly designing the device.

![Figure 6](image)

Fig. 6. — Band structure of a quantum well without (a) and with (b) an applied electric field. Variation of the excitonic absorption spectrum of the quantum wells with the reverse bias on the diode (c). The device is made of five 12 nm CdTe quantum wells with 20 nm Cd$_{0.8}$Zn$_{0.2}$Te barriers, inserted in the space charge region of a Schottky diode.
3.2 PHOTOREFRACTIVE EFFECT IN BULK MATERIAL. — The interest of this effect has been outlined once again during this colloquium [14]. It has been observed for some time that II-VI semiconductors and specifically CdTe, could behave as efficient photorefractive materials because of their high electrooptic coefficient $r_{41}$ and refractive index $n$ [15]. For example CdTe at 1.5 $\mu$m has a figure of merit $n^3 r_{41}$ of 120 which is 2 to 3 times higher than that of GaAs:Cr or InP:Fe (50 to 60). In addition it has been shown recently that the introduction of vanadium in CdTe produces semi-insulating material useful for exploiting the photorefractive properties of CdTe [16].

3.3 BAND EDGE PHOTOREFRACTIVITY. — A multiquantum wells semiconductor heterostructure can be designed in such a way that the excitonic absorption band appears at some predetermined wavelength. As shown above the application of an electric field strongly modifies the absorption band. The fundamental coupling between the real and imaginary parts of the optical constants leads to variations of the refractive index. This basic phenomenon can
be used in a photorefractive device by converting light intensity modulation into electric field variation [17]. Again the large oscillator strength of these II-VI quantum structures, as well as the wide range of possible wavelengths appear as major advantages. A two beam coupling gain of 500 cm$^{-1}$ has been recently demonstrated at 600 nm [18] with CdZnTe compounds. Larger wavelengths can be reached: until 800 nm with CdZnTe and 1.5 $\mu$m or more with CdHgTe compounds.

4. Infrared lasers.

4.1 Horizontally Emitting Lasers. — This is the usual configuration of solid state semiconductor lasers. The cavity is of Fabry-Pérot type. It is obtained by cleaving two (110) facets containing the [100] growth direction. The light is guided in the horizontal plane by index variation along the growth axis. The CdHgTe compounds are well suited to the conception of structures of this type because the refractive index and the bandgap vary rapidly with the composition, while the lattice parameter variation is small.

The composition and index profiles of a separate confinement heterostructure (SCH) laser are reproduced in figure 8 for a Cd$_{1-x}$Hg$_x$Te device. The central active layer ($x = 0.5$) is sandwiched between two $x = 0.7$ barriers. The cladding layers are almost pure CdTe ($x = 0.95$). The corresponding values of the refractive index at 2 $\mu$m are respectively 2.7, 2.9 and 3.3. The SIMS analysis of the actual structure grown by MBE is shown in the lower part of the figure. With this structure it is possible to obtain stimulated emission up to room temperature, under optical pumping [19] as shown in figure 9. The dashed line is the c.w. low power excitation (30 W/cm$^2$) while the full line corresponds to the pulsed excitation (30 kW/cm$^2$). The characteristic features of the stimulated emission are visible up to room temperature: spectral narrowing, Fabry Pérot cavity modes, directivity.

More sophisticated structures of the GRINSCH type have also been grown [20]. The possibility of making injection lasers with CdHgTe has been recently demonstrated, for the 3 to 3.5 microns range [21, 22].

Fig. 8. — Schematic cross section of a Separate Confinement Heterostructure for the infrared and variation of the refractive index (a). The secondary ions mass spectroscopy (SIMS) analysis of the mercury content is given in (b).
Fig. 9. — Emission spectrum of a CdHgTe laser structure excited with a YLF laser at 1047 nm. The incident power is 30 W/cm² (dashed line) or 30 kW/cm² (full line). The emission spectrum of the barriers is given in the inset.

4.2 VERTICAL CAVITY SURFACE EMITTING LASERS. — This new laser concept uses an optical cavity which is made of two mirrors integrated during the device growth. The design and realization of the mirrors are then essential to the laser efficiency. The mirrors are generally of Bragg-type with the alternate growth of high and low-index λ/4 layers. The CdHgTe compounds are again well-suited to the preparation of such mirrors, for the reasons developed in the previous paragraph [23]. In particular the very small lattice mismatch between the layers allow to grow 300 to 500 nm thick layers without misfit dislocations. Figure 10 reproduces the structure of a mirror (upper part) — with pairs of Cd,Hg₁₋ₓTe layers where x is alternatively 0.5 and 0.95. The lower part of the figure gives the theoretical and experimental transmission spectra. The difference between the two curves, on the high energy side is due to the onset of the absorption by the mercury rich layers. At the central wavelength the transmission is only of 3 % corresponding to a reflectivity of 97 %. This is a satisfactory order of magnitude for making a laser cavity, if the intracavity gain is large enough to overcome the various losses. The main problem comes from the short active length (~ 1 micron). A large specific gain of more than 200 cm⁻¹ is then required. Another difficulty of this structure is the electrical resistance of the mirror regions, even if they are heavily doped, since each interface introduces an electrical barrier. In despite of the difficulties, such a vertical cavity surface emitting laser would bring useful features and help integrating optoelectronic devices.
substrate

10 periods

high index

low index

x=0.95

265 nm

x=0.5

225 nm

Fig. 10. — Schematic of a Bragg mirror (a) made of 10 \( \lambda/4 \) pairs of index 2.83 and 3.23. The transmission spectrum of the mirror (b) shows the reflectivity band between 430 and 520 meV. The theoretical spectrum is given for comparison. The high energy part of the experimental spectrum is dominated by the absorption of the mercury rich layers (\( x = 0.5 \)).

5. Conclusion.

The molecular beam epitaxy of II-VI semiconductors is now a mature technique with which it is possible to design and grow a large variety of structures whose thickness may range between monolayer and several microns. The available compounds open the way to many optoelectronic devices, for almost any wavelength in the visible or infrared. We have given some examples of new devices which take advantage of the specific properties of molecular beam epitaxy and which are already, or will be soon, available:

- lasers for the visible;
- electrooptic modulators for the visible and the near infrared;
- photorefractive materials;
- infrared lasers with in plane or vertical emission.

The progress in the growth technology, the control of doping and interfaces should allow to produce devices precisely designed to meet the application requirements.
References