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BERYLLIUM CHALCOGENIDE ALLOYS FOR VISIBLE LIGHT EMITTING AND LASER DIODES

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Abstract. We give a brief overview of the current advances in the development of green light emitting and laser diodes (LEDs and LDs). We review problem of rapid degradation of LDs based on II-VI material family. We cover recent advances in this area stressing the development of novel beryllium chalcogenide alloys. We discuss an increase in the lifetime of beryllium-containing light emitters recently reported by several research groups. These results demonstrate that beryllium chalcogenide alloys are attractive for the design of visible light emitters.

1. INTRODUCTION

There is a significant technological interest in light emitting and laser diodes (LEDs and LDs) operating in the visible region of the spectrum. The possible areas of application include high-density optical data storage, fiber-optical communication, xerography, underwater measurements, medical imaging, and projection display fabrication. In particular, high-definition and high brightness displays will benefit from the semiconductor laser technology. We present the 1931 CIE chromaticity diagram in the Fig. 1. From this figure it is evident that the development of red (~ 680 nm), green (~ 520 nm), and blue (~ 420 nm) LDs will allow fabrication of full-color projection displays.

Significant success has been recently achieved with the group III – nitride semiconductor material family. Pure - blue LDs (~ 405 nm) with the lifetime of ~ 10000 hours under the CW room-temperature (RT) operation were reported in 1998 [1]. A few years later $Al_xGa_yIn_{1-x-y}N$ – based LDs were further developed to the stage of practical use [2]. However, to shift the emission to the longer wavelength it is necessary to increase the In content of the quantum well (QW) region. This introduces serious In compositional fluctuations and phase separation resulting in a gain broadening, a rapid increase of the threshold current density, and a fast device degradation [3].

The group III – phosphide materials are currently used for the red LDs operating in the 630 – 670 nm wavelength range. However, due to the specific behavior of the $Al_xGa_yIn_{1-x-y}P$ band structure, the $Al_xGa_yIn_{1-x-y}P$ – based LDs operating at the shorter wavelength exhibit a significant increase of the threshold current density and a decrease of the differential quantum efficiency [4]. The band gap of the $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ alloy , that is lattice – matched to GaAs at this composition, exhibits a direct – to – indirect band gap transition (E_g ~ 2.3 eV) when the Al content reaches 50% (x ~ 0.5) . While the direct band gap continues to increase with the Al content (x), the indirect band gap remains constant [5]. This significantly decreases quantum confinement in the

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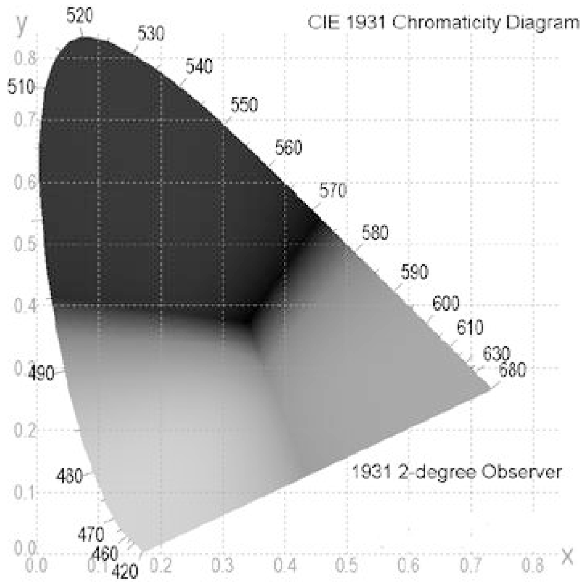

Fig. 1. The 1931 CIE chromaticity diagram.

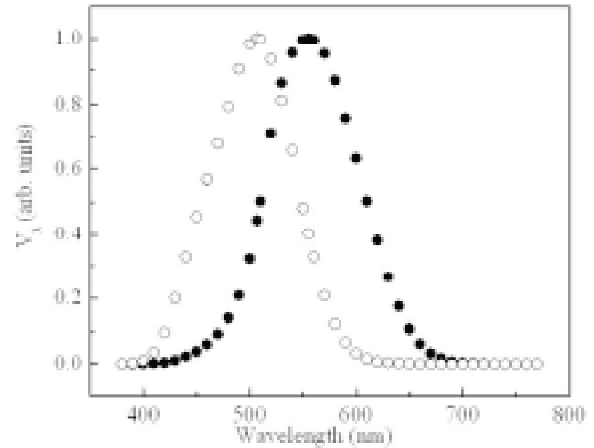

Fig. 2. The spectral luminous efficiency of a photopic (solid symbols) and scotopic (open symbols) vision.

$Al_{0.52}In_{0.48}P/Al_xGa_yIn_{1-x-y}P$ QWs and increases carrier escape from the active region to the barriers.

Thus, there are no commercially available devices operating in the green region of the spectrum. As we have previously showed, green LDs are necessary to complete the arrangement of the full-color displays. Furthermore, this spectral region is important for many emerging technologies, such as the use of plastic – optical fibers that require green lasers to achieve lowest attenuation coefficient [6]. Green lasers are also of significant interest for pointing devices. Since human eye is mostly sensitive to the green luminescence, as shown in Fig. 2, green pointers are more attractive than currently available red ones. Necessity in green LDs for the listed above applications revises interest in II-VI wide band gap semiconductors that cover the whole green spectral region.

2. DEVELOPMENT OF II-VI LIGHT EMITTERS

The band gap energy and the lattice constant of the semiconductors have to be considered to choose the optimum material for LD fabrication. Fig. 3 shows some of the important compound semiconductors giving their band gap energies and lattice constants. From the Fig. 3 it is evident that II-VI semiconductors widely cover the whole visible spectrum and are lattice-matched to many commercially available substrates including GaAs, InP, and Si. This stimulated study of II-VI wide band gap semiconductors in the early 90s. The $Zn_xCd_{1-x}S_{1-y}Se_y$ alloy attracted particular attention, since it can be grown by molecular beam epitaxy (MBE) with high crystalline quality closely lattice matched to GaAs [7]. Although the RT lasing from the $Zn_xCd_{1-x}Se/ZnSe/ZnS_{1-y}Se_y$ heterostructures under the pulsed current injection was reported in 1991, a CW operation was problematic due to the insufficient quantum confinement [8]. This problem was solved two year later by the development of $Mg_{1-x}Zn_xS_{1-y}Se_y$ alloy [9,10]. Next, ZnTe/ZnSe super lattices (SLs) were introduced as a p-type contact layer [11]. These developments led

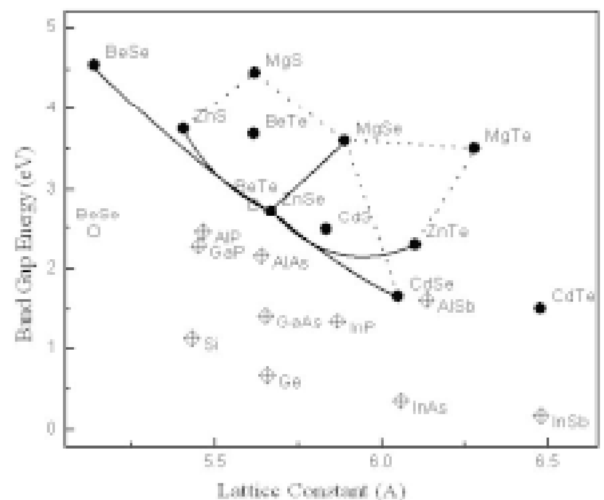

Fig. 3. Band gap energy and lattice constants for important compound semiconductors. The II-VI semiconductors are shown with solid (direct band gap) and open (indirect band gap) circles. The III-V and IV semiconductors are shown with diamonds.

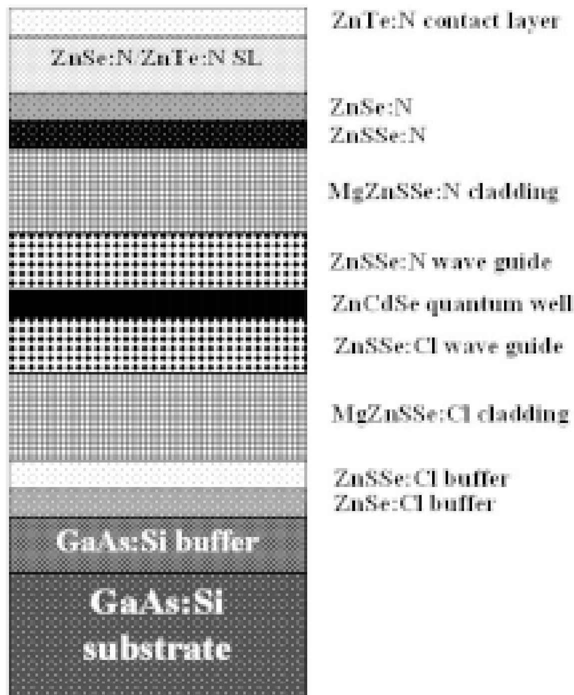

Fig. 4. The schematic structure of a $Zn_xCd_{1-x}Se/ZnS_{1-y}Se_y/Mg_{1-x}Zn_xS_{1-y}Se_y$ laser diode.

to a 400 - hour - long CW RT operation of $Zn_xCd_{1-x}Se/ZnS_{1-y}Se_y/Mg_{1-x}Zn_xS_{1-y}Se_y$ laser (the schematics is shown in Fig. 4) reported in 1998 by SONY corporation [12].

Despite these achievements, the lifetime of the II-VI LDs was not high enough for commercialization. The degradation mechanism of $Zn_xCd_{1-x}Se/ZnS_{1-y}Se_y/Mg_{1-x}Zn_xS_{1-y}Se_y$ LDs was studied. It was found that both extended defects originating at the III-V/II-VI interface [13] and point defects in the active region [14] were responsible for the early device degradation. The degradation was enhanced by the defect recombination of the electron-hole pairs [15]. Therefore, when several research groups explored novel approaches, they were aiming to increase the lifetime of II-VI LDs both through the development of more rigid alloys and by the improvement of the III-V/II-VI interface.

3. BERYLLIUM CHALCOGENIDE ALLOYS FOR II-VI LIGHT EMITTERS

Beryllium chalcogenide alloys, such as BeSe and BeTe, attracted a lot of attention because of their strong lattice hardness and high degree of covalent bonding, when compared to the other II-VI compounds [16]. It was expected that the introduction of the beryllium chalcogenides into II-VI LDs would suppress defect generation and propagation and will increase the device lifetime.

Due to the low vapor pressure, the Be effusion cell has to be operated above 1000 °C during the MBE growth of beryllium chalcogenide alloys. Such a high temperature is quite unusual for the MBE growth of II-VI alloys. All other cells and the substrate heater are operated between 150 °C and 400 °C making inevitable a pronounced heating of a semiconductor wafer by thermal radiation from the Be cell.

In spite of this problem, the results of the MBE growth of beryllium containing alloys were promising from the early stage. The defect density of the II-VI epilayers grown on GaAs was significantly improved either by the deposition of a few - monolayer thick BeTe interfacial layer [17] or by a Be-Zn co-irradiation performed at low temperature prior to the II-VI growth [18]. The $Be_xZn_{1-x}Se$ films grown with a few percents of Be exhibited high crystalline quality as was indicated by a narrow X-ray rocking curve of ~ 20 arcsec, low etch pit density of mid 10^4 cm^{-2}, and a sharp emission line with the full width at half maximum of 2.5 meV at 13K [18]. The improvement in the crystalline quality was due to the prevention of the formation of Ga_2Se_3 islands at the III-V/II-VI interface and a consequent decrease of the stacking fault density [17,18]. The Young's modulus and the c_{11} elastic modulus of $Be_xZn_{1-x}Se$ alloy were increasing with the BeSe content, giving a direct evidence of the lattice hardening properties of BeSe [19,20]. Therefore, the formation energy for the stacking faults in $Be_xZn_{1-x}Se$ is expected to be higher than in ZnSe, resulting in a lower defect density.

Since BeSe has a small lattice constant and large band gap energy, it is a very good candidate to replace ZnS in the $Mg_{1-x}Zn_xS_{1-y}Se_y$ alloy. It is important to note that the MBE growth is more controllable and reproducible when an alloy contains several metals and a single nonmetal, rather than several nonmetals. For example, during the MBE growth of $Mg_{1-x}Zn_xS_{1-y}Se_y$ the sticking coefficient of sulfur depends strongly on the substrate temperature, making it extremely difficult to avoid compositional fluctuations. MBE growth of $Be_xZn_yMg_{1-x-y}Se$ was already performed and the films exhibited high crystalline quality with an extremely narrow X-ray rocking curve of ~ 20 arcsec and an etch pit density below 5000 cm^{-2} [21]. The $Be_xZn_yMg_{1-x-y}Se$ was also successfully grown on Si [22] and GaP substrates [23], making possible future integration of the II-VI materials with the mature Si – based technology.

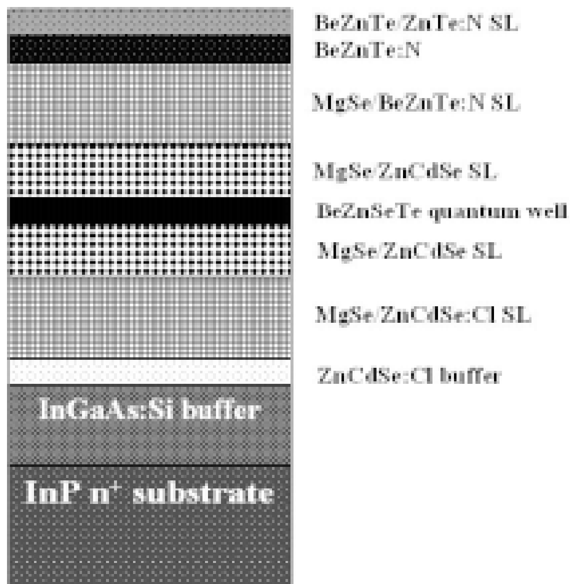

Fig. 5. The schematic structure of a $Be_xZn_{1-x}Se_yTe_{1-y}$ – based light emitting diode.

In order to strengthen the active region in LDs, $Be_xZn_yCd_{1-x-y}Se$ and $Be_{1-x}Cd_xSe$ alloys were proposed as an alternative to the $Zn_xCd_{1-x}Se$ alloy. These alloys were grown by MBE on InP and GaAs substrates [24-28] and in a bulk crystal form [29]. Optical properties of the QWs with the $Be_{1-x}Cd_xSe$ active layer were studied [30]. The $Be_{1-x}Cd_xSe$/ZnSe optically pumped lasers [27,28] and LEDs [31] were also demonstrated. The lifetime of the LED under the CW RT operation exceeded 15 hours, indicating feasibility of $Be_{1-x}Cd_xSe$ as an active layer.

The BeTe is an indirect semiconductor that is closely lattice matched to GaAs ($\Delta a/a_0$ = 0.6%). A ternary alloy of BeTe and ZnTe, $Be_xZn_{1-x}Te$ attracted much interest due to its possible application in optoelectronic devices. The $Be_xZn_{1-x}Te$ was grown with a high crystalline quality on GaAs and InP substrates and was doped p-type to carrier concentration levels in excess of 10^{19} cm^{-3} [32-35]. Similar to BeTe/GaAs [17], deposition of $Be_{0.5}Zn_{0.5}Te$ interfacial layer on InP significantly decreased defect density of the subsequently grown II-VI epilayers [36]. Since the band gap of $Be_xZn_{1-x}Te$ can be tuned from 2.8 eV to 4.1 eV, by adjusting BeTe content, it became a natural choice for a transparent p-type contact layer in the green LEDs and LDs. To fully exploit $Be_xZn_{1-x}Te$, its optical [37,38] and vibrational [39,40] properties were systematically studied by complementary techniques.

The BeTe/ZnSe and $Be_{0.5}Zn_{0.5}Te$/MgSe ($Be_{0.5}Zn_{0.5}Te/Zn_{0.5}Cd_{0.5}Se$) short period SLs were grown lattice - matched to GaAs and InP substrates, respectfully [41,42]. These were type-II SLs with a spatially indirect transition in which electrons and holes were separately confined in different regions. That is, for BeTe/ZnSe holes were in BeTe and electrons were in ZnSe. The BeTe/ZnSe and $Be_{0.5}Zn_{0.5}Te$/MgSe SLs were used as a p-type cladding layer in the green LEDs grown on GaAs and InP substrates, respectfully [31,43]. The $Be_{0.5}Zn_{0.5}Te$/MgSe p-type cladding layer significantly improved degradation characteristics. The lifetime of a device with a $Zn_{0.5}Cd_{0.5}Se$ well layer exceeded 130 hours under the CW RT operation [43]. Further optimization of the device structure involved development of a $Be_xZn_{1-x}Se_yTe_{1-y}$ alloy for a more robust active layer [44]. The lifetime of the $Be_xZn_{1-x}Se_yTe_{1-y}$ – based LED (the schematic is shown in Fig. 5) exceeded 2500 hours, demonstrating a significant improvement in the device reliability [45]. Current injected lasing from LDs with $Be_{0.5}Zn_{0.5}Te$/MgSe cladding layer was also achieved [46], indicating feasibility of these materials for LD application.

4. CONCLUSION

In conclusion, beryllium chalcogenide alloys have recently attracted much attention because of their strong lattice hardness and high degree of covalent bonding. Beryllium containing alloys were grown by MBE with high crystalline quality. Their further incorporation in LEDs significantly enhanced lifetime of the devices. We believe that further research in this field can solve problem of rapid device degradation historically associated with II-VI material family.

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