Characterization of low - pressure MOVPE Grown znmgsse heterostructures for Optoelectronic device applications

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Abstract : - The optical and electronic transport properties of ZnSe/ZnMgSSe/GaAs diode structure grown by low pressure metalorganic vapour phase epitaxy (LP-MOVPE) system for optoelectronic device applications are presented. A binary ZnSe buffer layer about 50 nm was introduced between the GaAs substrate and the ZnMgSSe quaternary layer to yield a significant increase of the structural quality of the device. Photoluminescence(PL) measurements were used to verify the grown ZnMgSSe layer properties. The spectra showed high composition homogenity for samples with Mg and S concentrations of about 15 % and 20 % respectively. Current - voltage (I - V) and frequency dependent capacitance - voltage (C-V) measurements were used to verify the electrical characteristics of the grown devices. As a result of using our proposed structure turn on voltage of the junction diode was decreased to about 7V, and a remarkable reduction by about 1V after rapid thermal annealing was detected. The rapid increase of capacitance with forward bias suggest that carrier trapping is a dominant mechanism in these devices.The relationship between the Mg concentration of the ZnMgSSe quaternary layer and the electrical properties of the device is investigated.

Key_Words: - Optoelectonic device applicatinos- MOVPE grown ZnMgSSe heterostructures

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1 Introduction

The use of blue-green lasers in audio compact discs and CD-ROMs could increase the information density by over five times. These enhanced density systems with erasable capability promise to be a major part of the next generation of multimedia systems. The blue-green lasers from II-VI semiconductors are expected to be a key component.

Major strides have been made recently in developing blue light emitting devices principally based on the zinc chalcogenide semiconductors. An important factor in these advances has been a continuous improvement in material quality as well as the introduction of innovative approaches to doping. These developments have brought with them electrical materials characteristics that are the core of this development, and the focus lies principally on the zinc chalcogenides and the factors that limit transport in these materials. One of the problems in epitaxial growth of ZnSSe ternary compounds is the lattice mismatch between the GaAs substrate and the ZnSSe heterostructure with high S content. The unrelaxed strain as well as stacking faults and dislocations in the region of lattice relaxation decrease the crystalline quality and radiative efficiency. One of the possibilities to overcome these disadvantages is the use of ZnMgSSe quaternary compounds which allow to grow lattice matched layers [1-2].

LP-MOVPE technique, which is a growth technology oriented for mass production, is a good choice to grow ZnMgSSe layers due its enhanced composition control for quaternary semiconductor alloys . However only few reports on using this technique have yet been published [3] , and the need of the quaternary $Zn_{1-x}Mg_xS_ySe_{1-y}$ (x , y ~ 0.15) cladding and guiding layers for separate confinement heterostructure (SCH) or double heterostructure (DH) lasers on the basis of ZnSe as an active layer has been reported [4]. This compound offers the possibility of independently tuning the bandgap between 2.7 (ZnSe) and 4.5 eV (MgS) , and a lattice constant between 0.555 nm (ZnS) and 0.585 nm (MgSe) respectively, and hence it allows the lattice matched growth on GaAs substrate [5] . Therefore it is commonly thought that its use in DH or in SCH will enable a better room temperature performance of these optoelectronic devices[6] .

Regardless of the growth techniques, however, the electrical characterization of such devices is complicated by the problems encountered form ZnMgSSe layer. This material, although proven to be useful in achieving room temperature lasing, has some drawbacks. Magnesium is a very reactive metal and is not available in ultra-high purity. Also, ZnMgSSe contains many structural defects that tend to deteriorate the material under lasing conditions. Yet another problem is p-type doping due to self-compensation which limits the net carrier concentration to about 1 x 10^{17} cm^{-3} in ZnMgSSe. Due to all these difficulties , the ZnMgSSe cladding layer must be thin[7].

In this paper we report on the growth of n-ZnSe/ZnMgSSe/ZnSe/GaAs diode structures using LP- MOVPE technique . We introduced a binary ZnSe buffer about 50 nm between the GaAs substrate and the ZnMgSSe quaternary layer which has shown to yield a significant increase of the structural quality as a result of lattice matching between the layers.

The relationship between the Mg concentration of the ZnMgSSe quaternary layer and the electrical properties of the device will be investigated.

2 Experimental

ZnSe/ZnMgSSe/ZnSe structure was grown on an n-type (100) GaAs substrate by LP- MOVPE. For the reproducible deposition of ZnMgSSe and ZnSe alloys we use the precursor combination dimethylzinc ((DMZn (TEN)) , ditertiarybutyl-selenide (DTBSe), ditertiarybutylsulphur (DTBS) and bismethylcyclopentadienylmagnesium $((MeCp)_2 Mg)$. The process temperature is 330°C and the total reactor pressure is 400 hPa. This combination allows the reproducible adjustment of the alloy composition maintaining high crystal homogenity and almost lattice matched growth . All samples were grown in a horizontal AIX - MOVPE syetem . The growth rate has been adjusted to 0.7
μm/h.The standard etching in HF (40%) was used to remove the native oxide from the GaAs substrate surface. Photoluminescence measurements with 0.015 W HeCd-laser (λ = 325 nm) radiation were performed. The layer compositions were verified by electron probe micro analysis (EPMA).

Standard ohmic contacts (Ni/Au-Ge/Ni) were evaporated onto the back of the GaAs substrate and annealed at 300 °C for 3 min.

Current - voltage (I - V) and frequency dependent capacitance - voltage (C - V) measurements were used to verify the electrical characteristics of the grown devices. The I - V characteristics were measured using HP 4145 B parameter analyzer. While C - V measurements were performed with HP 4192A impedance analyzer.

3 Results & Discussions

3.1 Photoluminescence Measurements

a key issue for successfully device applications of this structure (material system) is reduction of the density of crystalline defects in epilayers. For this purpose photoluminescene measurements were performed in order to investigate the correlation betwwen ZnMgSSe layer composition and the electrical properties of the grown devices , aiming at recognition of inherent material features and assistance in optimization of growth conditions.

The Mg and S concentration of the ZnMgSSe quaternary epilayers were varied between 0 and 0.2 , leading to various gap energies and lattice constants. In Fig.1 , the normalized photoluminescene spectra of the near band edge region of different ZnMgSSe samples with different Mg and S ratios are plotted for comparison.The shift of the band edge emission of the plots towards higher energy is in agreement with the incorporation of sulpher and magnesium concentrations in the samples.

By analyzing the alloy broadening of the band edge emission of the plots , we observe a good homogenity for Mg and S ratio of about 15 and 20 %

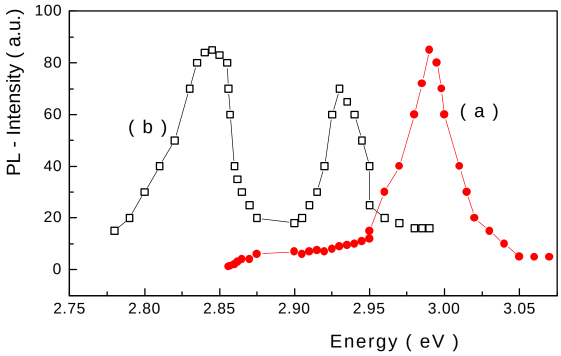

Fig.1. Photoluminescence spectrum of the near band edge r
of ZnMgSSe samples with different Mg concentration
(a)15% Mg 20 % S (b) 5% Mg 20%

respectively of the ZnMgSSe layer as indicated from the narrow bandwidth (inset a) . The well pronou-nced peak indicates that this layer is suitable for the growth of strain-balanced pseudomorphic structures, and consequently promises an enhanced electrical confinement.

On the other side, the epilayers with lower Mg concentration of about 5 % show a broadening and double peaks in spectra as observed in (inset b). This indicates an enhanced phase separation in ZnMgSSe layer. These effects have been found to be strongly depending on the epilayer strain status and growth interruptions especially at interfaces in heterostruc-tures[3].

Compared to samples grown using Molecular Beam Epitaxy (MBE) technique, Gerhard et al [8] recently reported a large peak separation of MgZnSSe epilayers by measuring rocking curves and reciprocal space maps. This peak separation cause a strong variation in the electronic properties of their samples , and they concluded that the peak separation is mainly caused by a composition variation in growth direction. These results confirm the high structural quality of our samples.

3.2 Current - Voltage Measurements

In order to explore the structural integrity of the device structures, the electrical properties also enter into consideration. Fig.2. shows the current - voltage (I - V) characteristics at room temperature measured over the range -15 to 20 V for LP- MOVPE grown samples. Turn on voltage of the junction diode without ZnMgSSe layer was about 17V as shown in the plot of sample (a). This large turn on voltage , which cannot be tolerated in a laser structure , is attributed to a high resistivity layer produced by misfit dislocations at the GaAs-ZnSe interface . However, this value is lower than the turn on voltage of about 20 V typical of a GaAs/ZnSe diode structure grown using MBE technique[9].

On the other side, turn on voltage of junction diode with ZnMgSSe layer (Mg = 15 % , S = 20 %) was about 7V as shown in the plot of sample(b). As can be observed the current increases rapidly, and reaches 10 mA at about 8 V as a result of using our proposed structure. The plot of log (I) vs bias voltage of the curves of Fig.2. exhibits different regions , we assign these transitions to different bandgap values as a result of device structure.This may be caused either by a composition change in the vertical direction (growth direction) or by different strain states in the epilayers. The data from the plots were used to calculate the ideality factor, n ,which yields information on the current transoprt process . These values are unreasonably high, but considering the influence of a series resistance of the layers more reasonable values are obtained. The ideality factor for sample(a) was $n \approx 9.5$ and for the sample(b) $n \approx 3.8$ where a remarkable improvement was found. In both devices the tunneling current dominates the measured (I - V) characteristics in the high voltag region. Stanzl et al [10] , reported higher values for the ideality factor for their ZnSe-based grown devices. The ideality factor for a device grown using MBE technique was $n = 59$ and for a device grown using MOVPE was $n = 55$.

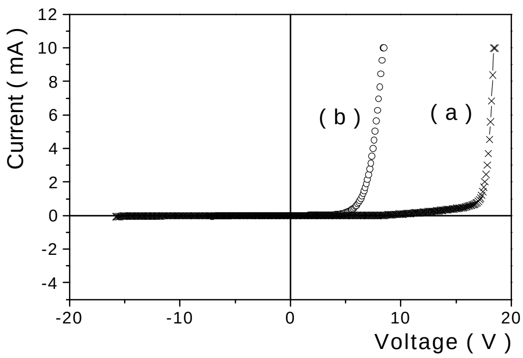

Fig.2. Effect of ZnMgSSe layer on I - V characteristics
of diode structure (a) without ZnMgSSe .
(b) with ZnMgSSe layer (15 % Mg , 20 % S).

They reported a remarkable improvement for ZnSSe based diodes, which exhibit a steeper slope for forward bias with ideality factor n = 36 . This difference in ideality factor , can be correlated with specific interface structure as well as fabrication-induced defects.

Our initial investigation of the effect of rapid thermal annealing (RTA) on the I - V characteristics can be observed in Fig.4. The measurements were performed after RTA of sample (b) in vacuum at a temperature of 400°C for a duration of 60 s. A remarkable reduction in the turn on voltage by about 1V after RTA can observed as shown in curve (II). This comparison highlights that RTA seem to be critical and strongly affects the I - V characteristics

An important achievement was made by which we could reduce the turn on voltage down to the 6V

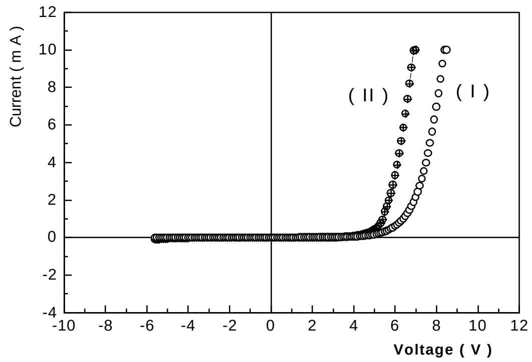

Fig.3. Effect of RTA on I - V characteristics of diode(b)
(I) Before RTA (II) After RTA

range from voltages that previously used to be over 10 V. We hope to see even better results after optimization of heat treatment of the diode structure. Such a reduction in the turn on voltage is required for improving these devices in order to increase the lifetime.

The results of a continuing effort to understand the electrical properties of this diode structure will be presented in tne next section.

3.3 Capacitance - Voltage Measurements

A set of C-V curves at two different frequencies for sample (b) after RTA is shown in Fig.4. The device showed a large frequency dependence of capacitance which is indicative of the presence of a wide range of distributed time constants values associated with defect centers, possibly with energies distributed within the entire band gap of the ZnMgSSe material . Also, a rapid increase of capacitance with forward bias at 10 KHz suggest that carrier trapping is indeed a dominant mechanism in these devices.

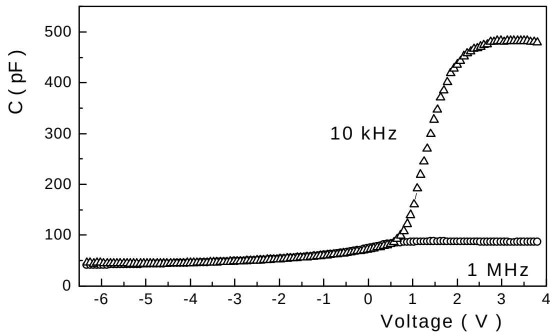

Fig.4. Frequency dependence of C - V curves of sample (b) after RTA.

The results for the net free carrier concentrations obtained from the standard analysis of the slope of $1/C^2$ versus voltage curve at different frequencies are different . The obtained values was not higher than 8 x 10^{17} cm^{-3}, one likely possibility is that Mg creates deep localized states which trap holes in ZnMgSSe[11]. In fact, the net acceptor density may be lower than that, an estimate of about $1x10^{17}$ cm^{-3} for Mg concentration of 10 % has been reported for MBE grown structure[9]. Although that range are suitable for the injection layers in LDs , it would be desirable to achieve much larger net acceptor density.

Therefore we believe that we can establish reliability of the ZnMgSSe-based laser diodes by eliminating the pre-existing defects , and by slowing down the gradual degradation through reducing point defects ·

Fig.5. shows a capacitance - voltage of a typical device measured at different frequencies. It is observed that the capacitance decreases with the reverse bias and becomes independent of the applied voltage for very high frequencies (> 1 MHz) . We might expect the whole thickness of the device to be depleted and this would correspond to a capacitance equivalent to the geometrical capacitance of the device. Similar observation has been reported elsewhere [12] for different diode structures grown by MBE technique, and there are various models explaining such phenomena in devices which are formed on semiconductors with trapping levels in the energy gap.

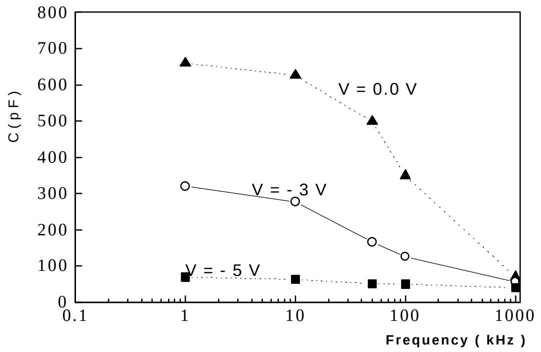

Fig.5. Capacitance versus frequency for different bias voltages for a typical device.

Our investigations clearly demonstrate that the Mg concentration in the ZnMgSSe layer and influence the effective doping concentration as well as the trapping behaviour of the device.

4 Conclusions

LP-MOVPE growth technique allows the deposition of quaternary ZnMgSSe layers with predictable lattice constants and bandgaps suitable for blue ZnSe-based laser diodes and other optoelectronic applications. These layers show a high degree of homogeneity especially at certain range of S and Mg concentrations. The introduction of a thin binary ZnSe buffer layer between the GaAs substrate and the quaternary ZnMgSSe layer has shown to yield a significant increase of the structural quality, and lattice matching in the studied structure. Electrical characterization highlights the importance of RTA on the I - V characteristics. An important achievement was made by which we could reduce the turn on voltage down to 6V range from voltages that previously used to be over 10 V. The capacitance of these diodes are highly frequency dependent which indicates the presence of defect states with a wide range of distributed energies in these devices. Further insight into the nature of the interface formation and changes of trap properties due to thermal treatment of the device are in preparation.

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