Superficies y Vacío ***9****, 253-255, Diciembre 1999*

Effect of a III-V buffer layer on the quality of ZnSe thin films grown by MBE on GaAs substrates

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In this work we present a study of ZnSe films grown on buffer layers of the ternary compounds $In_xGa_{1-x}As$ and $Al_xGa_{1-x}As$ by means of photoreflectance (PR), and photoluminescence (PL) spectroscopies and transmission electron microscopy (TEM) . The buffer layers of the ternary compounds were grown by molecular beam epitaxy (MBE) employing concentrations with $0.01 < x < 0.3$ and thickness of 5000 Å. The films of ZnSe were grown by MBE in a separate II-VI system with a thickness of 6000 Å. The measurements of PR allowed us to determine the energy value of the ZnSe band gap, the magnitude of the internal electric fields, and to evaluate the quality of the buffer layers and the ZnSe film. The intensity and width of the excitonic related peaks in the PL spectra and the presence of lines related with defects allowed us to asses the crystalline quality of the films. TEM results have a good correlation with the optical spectroscopies showing that the better samples are those grown on buffer layers of $Al_{0.01}Ga_{0.99}As$ and $In_{0.01}Ga_{0.99}As$.
PACS: 78.20. Jq, 78.55.Et, 81.15.Hi.

1. Introduction

ZnSe has been considered as a promising material for optoelectronic applications in the blue-green region of the visible spectrum. There have been several efforts related to the production of electroluminescent diodes and laser devices [1,2]. In the ZnSe based laser devices the emission is produced in $Zn_{1-x}Cd_xSe$ quantum wells within ZnSe barriers. GaAs substrates have been commonly employed. It has been found that the effect responsible for the degradation of the devices is the generation and propagation of defects which finally degrade the quantum wells[1-4]. Several reports have shown the existence of a correlation between degradation and pre-existent defects at the ZnSe/GaAs interface. In this case defect generation is due to the inherent physical and chemical differences associated to the heteroepitaxial growth of ZnSe on GaAs [5]. There are two principal problems which have an important effect on defect generation: i) The 0.27 % lattice mistmatch between the ZnSe and GaAs, which produce a critical thickness of around 1700 Å [6] and ii) the excess of Ga on the substrate surface, produced during the oxide desorption necessary to substrate preparation, giving place to Ga segregation toward the film surface during the ZnSe growth[7,8]. Then, in order to improve the crystalline quality of the ZnSe thin films it is important to develop methods to reduce or eliminate the above mentioned problems [9]. In this work we present the results on the optical properties and interface-defect characterization of ZnSe films grown on $Al_{1-x}Ga_xAs$ and $In_{1-x}Ga_xAs$ buffer layers grown by molecular beam epitaxy (MBE) on GaAs(100). The films were studied by cross-sectional transmission electron microscopy (TEM); and photoreflectance (PR) and photoluminescence (PL) spectroscopies. In order to reduce the effect of the lattice mismatch between GaAs and ZnSe we employed the $In_{1-x}Ga_xAs$ buffer layer with x=0.01, with this In concentration there is a matching with the ZnSe lattice parameter, avoiding the generation of dislocations at the interface ZnSe/$In_{1-x}Ga_xAs$[10]. To reduce the Ga segregation toward the ZnSe surface, we proposed to use a $Al_{1-x}Ga_xAs$ buffer layers based on the fact that it is more difficult to break apart the chemical bonding of Ga in the ternary compound than in GaAs. In order to find out the adequate concentration of the Al buffer layers, concentrations of x = 0.01, 0,1 and 0.3 were employed

2. Experimental details

Buffer layers with thickness of 5000 Å of $In_{0.01}Ga_{0.99}As$ and $Al_xGa_{1-x}As$ with x=0.01, 0.1 and 0.3 were grown on GaAs (100). An As capping was deposited to prevent the formation of oxides on the buffer layer and was removed by annealing at around 500 ^{0}C before the growth of the ZnSe films. An independent II-VI MBE system was employed to growth ZnSe samples with a thickness of 6000 Å. The characteristics of the samples are presented in Table 1. The ZnSe films were deposited at 325 ^{0}C employing separated Knudsen cells for Zn and Se, with an equivalent pressure ratio of Zn/Se of 1/3 and growth rate of 1μm/h. Structural studies were carried out by cross sectional TEM. PR measurements were done at room temperature with the 6328 Å line of a He-Ne laser as modulator. PL was carried out with a 0.5 m monochromator employing the 3250 Å

TABLE 1. Characteristics of the studied samples.

Sample	Buffer layer	x	d_{ZnSe} (Å)	F_j x10^6 (V/m)
C277	$Al_xGa_{1-x}As$	0.3	6000	1.51
C275	$Al_xGa_{1-x}As$	0.1	6000	1.24
C240	$Al_xGa_{1-x}As$	0.01	6000	-
C241	$In_xGa_{1-x}As$	0.01	6000	-

x: In(Al) concentration in the buffer layer.
d_{ZnSe}: ZnSe film thickness
F_J :Buit-in internal electric field

line of a He-Cd laser as excitation source. Samples were cooled down at 14K employing a He open cycle cryostat.

3. Results and discussion

i) Photoreflectance

Figure 1 shows PR spectra of the samples. For all of them a signal from the GaAs substrate is observed around 1.41 eV. For samples C240 and C275 the PR signal coming from the AlGaAs buffer layer is also present. As the aluminum concentration increases there is an increase in the number of oscillations above the GaAs band gap. These oscillations are a manifestation of the presence of internal built-in electric fields coming from the surface and the interfaces and are termed Franz-Keldysh (FK) oscillations [11]. From the spectra characteristics shown in fig.1, it can be said that the interface substrate-buffer layer is determining the strength of the internal electric fields. The PR signal from the buffer layers and from the GaAs substrate are very close in samples C240 and C241 making difficult the identification of the oscillations associated with internal electric fields. For the sample with 10% of aluminum we observed the signal coming from the buffer layer at 1.53 eV, which corresponds to a real composition of 9 % [12]. In the PR spectrum corresponding to the sample grown on a buffer layer with a 30 % of aluminum the PR signal from the buffer layer is not clearly observed, probably because we have a greater amount of defects at the interface buffer layer-substrate. The strength of the internal electric fields was evaluated for sample C277 and C275 employing the

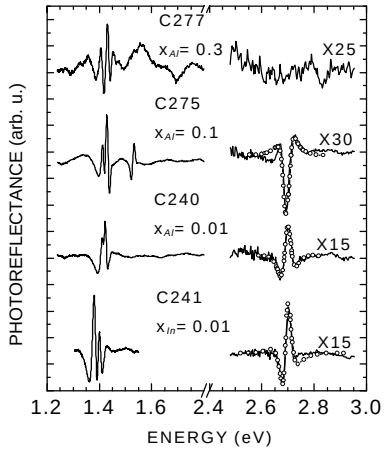

Fig.1 Room temperature spectra of the studied samples. The fitting to the ZnSe signal are shown with open circles.

TABLE 2. Fitting parameters for the photoreflectance signal of ZnSe.

Sample	E_o (eV)	Γ (meV)	E' (eV)	Γ' (meV)	ε_o x10^{-3}	ε' x10^{-3}	$S/(D^o,X)$
C277	-	-	-	-			42
C275	2.699	0.021	2.705	0.022	-0.548	2.741	26
C240	2.696	0.032	2.704	0.046	-2.193	2.193	3
C241	2.705	0.029	2.708	0.029	2.741	4.386	3

E'(E_0): ZnSe band gap; Γ´(Γ): line width; ε'(ε_o): strain
$S/(D^o,X)$: photoluminescence peak ratio

asymptotic model due to Aspnes and Studna and are shown in Table 1 [12].

The stronger electric field corresponds to the sample with the higher amount of aluminum in the buffer layer, this was expected because of the greater band offset between the buffer layer and the GaAs substrate when Al concentration increases. The PR signal associated with ZnSe is observed around 2.7 eV for all samples, except for that grown on the buffer layer with 30 % of aluminum. For samples grown on buffer layers with 1% of Al or In the PR signal of ZnSe is stronger and its line width narrower, reflecting the higher quality of this layers. The absence of the ZnSe signal for the sample with 30 % of aluminum in the buffer layer could be due to the pinning of the ZnSe bands due to deffects, this pinning could make more difficult the modulation of the ZnSe bands with the HeNe laser. We fitted the PR signal of ZnSe using the third derivative model due to Aspnes. The results are showed in fig. 1 as empty circles [13]. In order to obtain a reasonable fit it was necessary to employ two signalswith different band gap values. The values obtained are termed E_0 and E´ and reported in Table 2. We think that E_o and E' come from different strained regions [14], a more stressed region near to the ZnSe film surface (E'), and one partially relaxed close to ZnSe/buffer layer interface (E_0). The deformations associated with these values were obtained with the usual model of a tetragonal deformation [15], the values are reported in Table 2.

ii) Photoluminescence

In Fig. 2 are shown the PL spectra of the ZnSe films. We observe that the narrowest and more intense donor- bound excitonic related PL signals (D^0,X), around 2.8 eV, correspond to samples C241 and C240. The peak around 2.6 eV termed as the Y_o line, has been related to misfit dislocations [16]. The feature around 2.3 eV is associated to defects, and is called the S band; its origin is attributed to deep level emission related to undesirable defects or impurity-defect levels. Its relative intensity with relation to the excitonic features has been taken as a parameter of crystalline quality [17]. The ratios between the PL intensities of the S line and the (D^0,X) donor bound excitonic peak are shown in Table 2. The intensity of the S band decreases as the concentration of Al in the buffer layer decreases being the smallest for sample with x=0.01, indicating a better crystalline quality for this film [18].

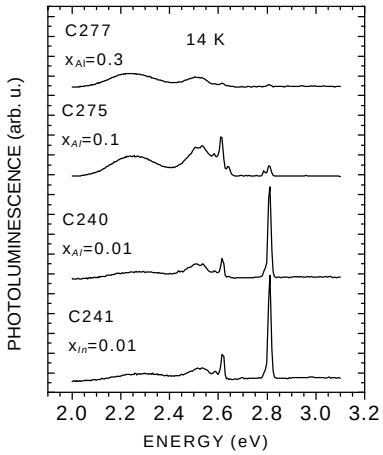

Fig.2 Photoluminescence spectra at 14 K of the studied samples.

These results are well correlated with those of photoreflectance discussed previously. The existence of a higher amount of defects for the sample with the $Al_{0.3}Ga_{0.7}As$ buffer layer could be associated to the fact that this sample was subject to a higher temperature in order to remove the As cap layer and Al related oxides, giving place to a rougher surface before the growth of the ZnSe.

iii) Transmission electron microscopy

Figure 3 shows cross-sectional TEM micrographs for the whole set of samples. We observe that samples C277 and C275 have the higher density of cristal defects (stacking faults). Sample C277 presents the roughest interface ZnSe-buffer layer. The sample C240 has a much lower density of defects compared with the previous one and a sharper interface. Finally, sample C241 is the best, with the sharpest interface and the lowest density of defects.

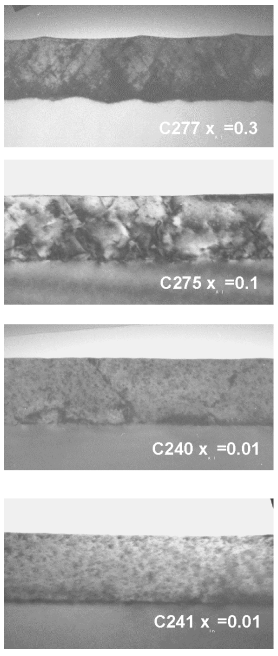

Fig.3 Cross-sectional TEM micrographs of the studied samples.

4. Summary.

The results of our study of ZnSe films grown on buffer layer of III-V ternary compounds by PR and PL spectroscopies and TEM, indicated that the better ZnSe thin film crystalline quality was obtained employing $In_{0.01}Ga_{0.99}As$ or $Al_{0.01}Ga_{0.99}As$ buffer layers. We observed a deterioration in the crystalline quality of the ZnSe films when growing on buffer layers with a higher concentration of aluminum probably because of the increasing roughness consequence of the higher temperature employed to remove the As cap layer and Al-related oxides.

Acknowledgments

This work was carried out with the partial support of CONACyT. The authors thank the technical support of Angel Guillen, Zacarías Rivera, and Hector Silva.

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