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THE RELATION OF DOMINANT DEEP LEVELS IN MOCVD $Al_xGa_{1-x}As$ WITH GROWTH CONDITIONS

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High quality undoped $Al_xGa_{1-x}As$ ($0 < x \leqslant 0.4$) has been investigated by transient capacitance, deep level transient spectroscopy and photoluminescence measurement techniques. The crystals were intentionally grown under different ambient conditions. Five dominant electron traps with ionization energy E_T ranging from 0.25 to 0.82 eV are present in crystals grown in the possible presence of moisture and oxygen. The density of four of these traps increase with increasing x suggesting the involvement of Al–O complexes in their formation. The density of the fifth, the well known EL2 electron trap, remains invariant. Only the EL2 center is identified in crystals grown in an oxygen- and moisture-free ambient. Two hole traps, with $E_T = 0.74$ and 0.87 eV are present in crystals grown at 690 °C, but are absent in crystals grown at 750 °C. They introduce light-sensitivity and compensation in the crystals and are removed by a short-term post-growth heat-treatment in a H_2 ambient. These centers are probably impurity-point defect complexes.

1. Introduction

The ternary semiconductor $Al_xGa_{1-x}As$ grown by metalorganic chemical vapor deposition (MOCVD) is an important material for the fabrication of solar cells and other opto-electronic devices. The advantages of this growth technique, pointed out by Bass [1], have now been adequately demonstrated. The conditions during epitaxial growth, i.e., the growth ambient and the source materials, play an important role in the incorporation of ubiquitous impurities and trap levels in the materials. In the present study we have made an attempt to correlate the origin of some dominant deep-level traps to MOCVD growth conditions.

2. Growth conditions and sample description

Single undoped epitaxial layers, 5–10 μm in thickness, and p–n junctions with undoped n-regions were generally grown at 690 and 750 °C with a V/III ratio of 10 and 20, respectively. Two sets of samples have been studied. The first set was grown in a reactor known to produce material with poor luminescence efficiency. The second set of samples were grown in a reactor in which the ambient is less susceptible to oxygen and H_2O contamination and which consistently produces crystals of high luminescence intensity. The free electron concentration in the samples studied varied in the range $(0.3\text{–}3.0) \times 10^{16}$ cm^{-3}.

Gold Schottky diodes were made on the epitaxial layers under a vacuum of 10^{-6} Torr and appropriate ohmic contacts to the Schottky and

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p–n diodes were made by evaporation and alloying.

3. Measurements

Photoluminescence measurements were made at 4.4 and 11.0 K on samples mounted in a strain-free manner in a liquid He cryostat. Excitation of variable intensity was provided by the 5145 Å line of an argon-ion laser and the photoluminescence was analyzed by a 0.5 m spectrometer. A liquid-N_2 cooled S1 photomultiplier tube was used as the detector. The spectral response of the photomultiplier was taken into account while analyzing the data. This is necessary since the energy gap of $Al_xGa_{1-x}As$ changes considerably in the composition range $0 \leqslant x \leqslant 0.4$. The values of x in the samples were determined from the energy position of the bound exciton peak.

Deep-level traps in the different layers with varying x were characterized by studying the thermal emission properties of the traps. both transient capacitance measurements at several fixed temperatures and DeepLevel Transient Spectroscopy (DLTS) were done to determine the thermal ionization energy and density of traps. Hole-traps in n-type materials were characterized by Optical DLTS (ODLTS) measurements. An externally triggered tungsten light source is used for these measurements. Trap densities were carefully measured by observing the peak height of the DLTS signal and the incremental transient capacitance change due to trap-filling in the transient capacitance measurements.

4. Results

Electron mobilities in the samples studied have been measured as a function of temperature [2]. Room temperature Hall mobilities are lower than high-quality LPE crystals by a factor of 1.5 to 2 for equivalent mixed-crystals compositions. The compensation ratio $(N_D + N_A)/(N_D - N_A)$ in the samples varied from 1.1 to 67.0, indicating the presence of large densities of unintentional acceptor-like impurities.

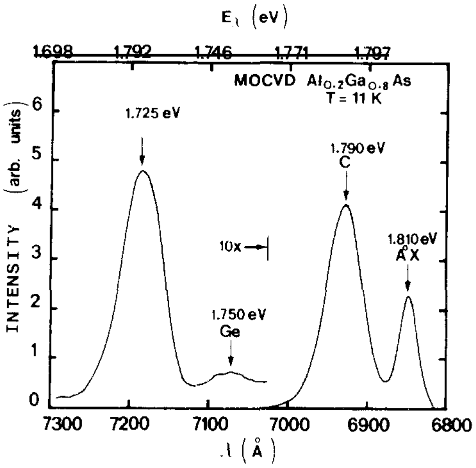

Fig. 1. Photoluminescence spectrum of undoped MOCVD $Al_{0.2}Ga_{0.8}As$ grown at 690 °C with a V/III ratio of ~ 20 in a well-sealed reactor. The measured value of the net donor concentration in the sample is 6.9×10^{15} cm^{-3}. The excitation power density is 10 W/cm^2 and the resolution is ≃ 2 Å.

The intensity of the edge luminescence, mainly consisting of one or more impurity-related transitions and a weak bound exciton related transitions was considered in the present study. A typical edge luminescence spectrum for a sample with $x = 0.2$ is shown in fig. 1, where the different identified acceptor species are indicated. The $A^\circ X$ peak at 1.810 eV is probably mainly related to C. The identity of the peak at 1.725 eV is not definitely known but is thought to arise from Mn. Carbon gives rise to the strongest peak in the edge luminescence of undoped samples, irrespective of the two different growth conditions mentioned above. Ge, Si and Zn are occasionally observed as weak transitions without any significant trend in their occurrence. Si and Zn-related transitions were identified by comparison with recently published data of other authors [3,4]. The shallow donor impurities are not identified.

The intensity of the edge luminescence was found to depend on the growth ambient and the Al content in the following way. The luminescence intensity is highest for samples grown in the reactor less susceptible to H_2O and oxygen contamination of the growth ambient. In the samples grown in the second reactor where H_2O and oxygen are possibly present in the growth ambient, the

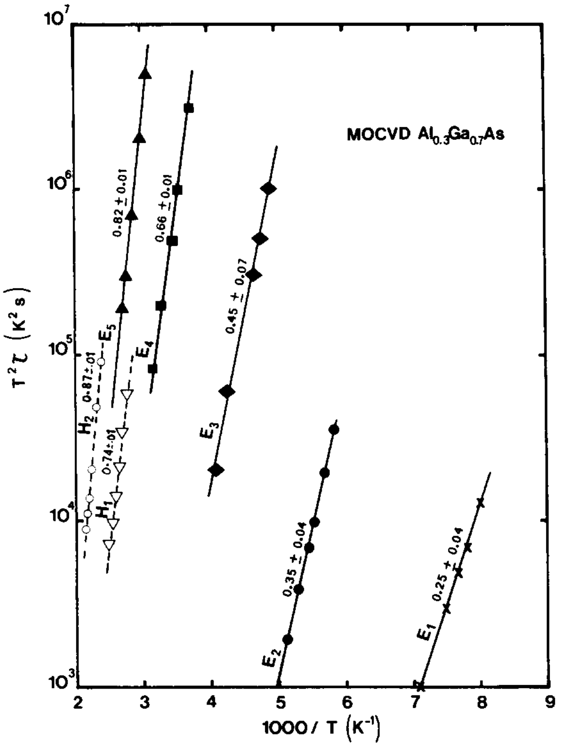

Fig. 2. Typical Arrhenius plots for $x = 0.30$ of dominant electron and hole traps in MOCVD $Al_xGa_{1-x}As$.

luminescent intensity was smaller and, in addition, decreased monotonically with increase of x.

The dominant electron and hole traps observed by us in the crystals studied are depicted in fig. 2. The electron trap with ionization energy $E_T = 0.82$ eV is the well-known EL2 center [5]. The characteristics of the electron and hole traps are given in table 1. Two trends of the electron trap densities are noticeable. In the samples grown with the possible presence of oxygen and H_2O in the reactor the electron trap densities are low for $x = 0.1$ and increase dramatically with increase of x. An exception is the EL2 trap, whose density remains almost invariant. We observed that the trap densities are uniform up to a depth of 2 μm below the surface. On the other hand, in crystals with $x = 0.1$ grown in an ambient free of oxygen and moisture all the electron traps, except the EL2 center, are practically absent ($N_T/n < 0.001$) and there is no significant trend in trap density with increase of x. The presence or absence of the hole traps is not dependent on the growth ambient and their densities are not dependent on the Al fraction x. However, the hole traps are usually absent in crystals grown at higher temperatures (750 °C).

Table 1
Representative characteristics of electron and hole traps in MOCVD $Al_{0.3}Ga_{0.7}As$; the measured value of n in the sample is 5.4×10^{15} cm^{-3}

Type	Trap label	E_T [a] (eV)	Capture cross-section σ_∞ [b] (cm^2)	N_T (cm^{-3})
Electron	E_1	0.25	1.0×10^{-20}	2.0×10^{15}
	E_2	0.35	5.2×10^{-20}	
	E_3	0.45	6.0×10^{-19}	1.0×10^{15}
	E_4	0.66	2.2×10^{-17}	8.0×10^{14}
	E_5(EL2)	0.82	4.4×10^{-16}	5.0×10^{13}
Hole	H_1	0.74	2.0×10^{-16}	4.0×10^{14}
	H_2	0.86	3.6×10^{-16}	7.0×10^{14}

[a] Mean values are indicated.
[b] Obtained from emission rate prefactor of Arrhenius equation.

5. Discussion

The density of all the electron traps, except the EL2 center, increases with increase of Al content when O is probably present in the growth ambient. In particular, the densities of the 0.35 and 0.25 eV traps become of the same order as the free electron concentration for $x \geqslant 0.3$. It is also seen that the intensity of the edge luminescence, for the samples in which the electron traps are present, is inversely related to the total density of the four electron traps. From our data, the approximate relationship is:

$$I_{PL}(\text{arbitrary units}) = 2.96\,(N_T/n)^{-0.53}, \qquad (1)$$

where I_{PL} is the integrated intensity of the edge luminescence in arbitrary units and N_T/n is the trap density relative to the measured free electron concentration n at room temperature. It may be reiterated that samples grown in the well-sealed reactor show negligible trap densities ($N_T/n < 10^{-3}$) and the integrated PL intensities are generally higher.

Since the trap densities increase with Al content in crystals grown in an ambient where oxygen and H_2O are possibly present, it is most likely that Al and O are both involved in the microstructure of these defects. In all probability one or more Al–O bonds contribute to form the microstructure of these complex defects. Post-growth annealing of the samples at 750 °C for 30 min under H_2 flow removed the 0.66 eV trap but not the other three traps under consideration. This suggests that the individual microstructure of the defects are different. The 0.66 eV trap may involve a native defect such as a vacancy. Wallis et al. [6] have observed five electron traps, including EL2, in MOCVD $Al_xGa_{1-x}As$ crystals which were grown in an ambient where oxygen was intentionally introduced. The activation energies of the traps identified by these authors are similar to the activation energies of the traps identified by us. This fact, and our observations described above reaffirm the role of Al–O bonds in the formation of these centers. Furthermore, our measurements indicate that some or all of these centers are responsible for the reduction in luminescence intensity of the samples. Measurements to study the microstructure of these centers are under way.

The density of the EL2 electron trap remains invariant with change of Al content in the mixed crystal. This fact and our previous observation [7] of the constancy of its thermal ionization energy with change of x suggest the association of the center with a Ga site. It is now believed that the center is probably an antisite defect involving a Ga site [8,9].

The two hole traps with $E_T = 0.74$ and 0.87 eV are only present in crystals grown at lower temperatures (690 °C) and they make the capacitance of Schottky diodes fabricated on the crystals extremely light-sensitive. A short-term post-growth heat treatment, as described above, anneals the traps and removes the light-sensitivity. We believe that larger number of point defects formed at lower growth temperatures form complexes with ubiquitous impurities and give rise to the observed hole traps.

6. Conclusions

Five dominant electron traps with thermal ionization energies E_T ranging from 0.25 to 0.82 eV and two hole traps with $E_T = 0.74$ and 0.87 eV have been identified in $Al_xGa_{1-x}As$ grown by MOCVD under varying growth conditions. The 0.82 eV electron trap appears with constant density in crystals with varying x. The density of four of the electron traps increase with Al-content when oxygen and moisture are possibly present in the growth ambient. These four traps are absent in crystals grown in purer ambients. This leads us to believe that one or more Al–O bonds form parts of the defect microstructure. The hole traps are observed only in crystals grown at lower temperatures and are annealed by short-term heat-treatment. They probably arise from complexes formed by the association of ubiquitous impurities with point defects.

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