Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 134-136 **D-2-6**

Efficient Er Luminescence Centers Formed in GaAs by MOCVD with Oxygen Codoping

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Er-doped GaAs is grown by a low-pressure MOCVD with and without oxygen co-doping. Optically efficient Er-oxygen complex centers are formed when a small amount of oxygen is present in the growth atmosphere. *In situ* monitoring of the surface morphology by light scattering from the growing surface with and without oxygen co-doping suggests that migration of Er atoms on the surface is pinned by the formation of an Er-oxygen complex. We speculate that this effect suppresses the formation of Er clusters and allows the formation of a high concentration of uniformly dispersed Er-oxygen complex centers that have a high optical efficiency.

1. Introduction

Impurity incorporation behavior such as atomic sites and solubility in solids are primarily governed by the thermodynamic characteristics of the impurities and the hosts. Quasi-equilibrium growth methods such as MBE and MOCVD, however, sometimes allow the formation of new impurity centers with concentrations above solubility limits. Rare earth (RE) atom-doped semiconductors are such materials because of their large atomic radii and ionic nature of REs. There has been increasing interest in semiconductors doped with optically active REs because of possible applications to optical devices.[1] Besides the practical applications, the RE-related spectra can be used to identify various atomic sites that REs occupy since their intra-4f-shell luminescence spectra reflect local surrounding atomic configurations.

An Er atom, which shows characteristic sharp luminescence around 1500 nm, has been doped in III-V compound semiconductors and silicon by many methods such as implantation, diffusion, LPE, MBE, and MOCVD.[2] However, the low solubility of the Er atoms in semiconductor hosts generally leads to segregation, forming Er-rich precipitates.[3] The appearance of many luminescence lines or broad lines indicates the simultaneous presence of various Er centers or inhomogeneous lattice distortion around Er, but the Er centers responsible for the luminescence have not been identified. Recently, we found that an optically efficient Er-oxygen complex luminescence center can be formed by MOCVD when a small amount of oxygen is added in the growth atmosphere.[4] In this talk, we present the results of *in situ* surface morphology monitoring by measuring a scattered light intensity during MOCVD growth of Er-doped GaAs with and without oxygen in the growth atmosphere. The changes in the morphology and the 4f luminescence suggest pinning of Er atoms on the growing surface by coupling with oxygen, which prohibits formation of Er clusters and allows formation of uniformly dispersed Er-O complex centers.

2. Experimental Results and Discussion

Er-doped GaAs epitaxial layers were grown by low-pressure (76 torr) MOCVD using triethyl gallium (TEG), arsine and isopropil tris(methyl-cyclopentadenyl erbium). The arsine-to-TEG molar ratio was 9 and the growth rate was 1.45 μm/h. Argon gas with 100 ppm of oxygen was used as an oxygen source. Photoluminescence (PL) measurements were carried out using an Ar laser (514.5 nm) as an excitation source and a cooled Ge p-i-n diode as a detector. For the measurements of concentration profiles by secondary-ion mass spectroscopy (SIMS), an O_2^+ ion was used as a primary ion for Er, and a Cs^- ion was used for carbon and oxygen. The *in situ* surface monitoring was carried out by irradiating an Ar laser beam (488 nm) onto the epitaxial layer surface in the reactor and detecting the scattered light intensity.

A typical spectrum due to intra-4f-shell transitions of Er-doped GaAs is shown in Fig. 1(a).

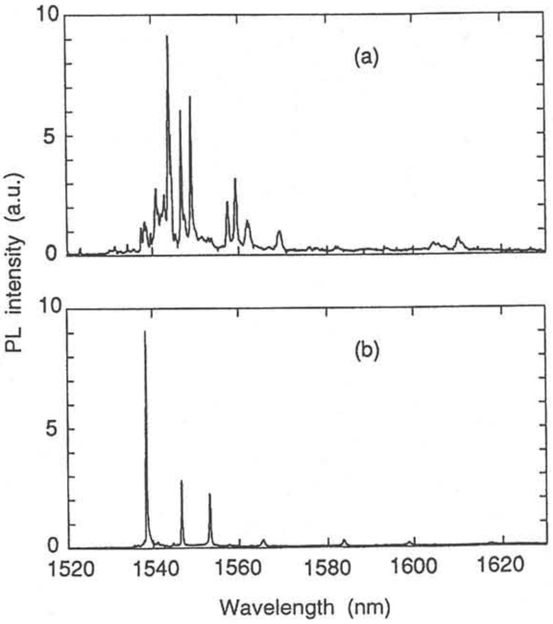

Fig. 1 PL spectra of GaAs:Er grown at 500°C (a) without and (b) with oxygen in the growth atmosphere. The peak intensity of the spectrum (b) is about ten times stronger than that of (a). The spectra were measured at 2 K.

When a small amount of oxygen is intentionally added to the growth atmosphere, the spectrum becomes simple and sharp as shown in Fig. 1(b). These luminescence lines are due to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} ion. A maximum of eight luminescence lines is expected from one type of Er ion. The luminescence spectrum observed in Fig. 1(b) comes from one type of Er luminescence center, which has been confirmed by measurements of PL excitation spectra by intra-4f photo-excitation.[5] On the other hand, the complex spectrum in Fig. 1(a) indicates the presence of Er with various atomic configurations. We can draw such a conclusion because intra-4f-shell PL spectra of Er dominantly reflect nearest-neighbor atomic configurations around the Er atoms due to good shielding of the 4f-shell electrons by the outer closed-shell electrons.

Figure 2 shows the result of a surface monitoring experiment. The vertical axes are the flow rate of argon gas containing oxygen, the scattered light intensity during the growth, and the carbon and oxygen concentrations in the epitaxial layer. The horizontal axis is the distance from the substrate/epi-layer interface. Oxygen was intentionally injected into the reactor in regions *A* and *C*, but not in region *B*. The epitaxial layer surface retains a smooth morphology in region *A* but gradually changes to a rough surface in region *B*. But when oxygen is injected into the reactor again, the surface becomes smooth again, as seen in region *C*. Carbon is coupled with Er in MOCVD-grown Er-doped GaAs.[6] When oxygen is introduced into the growth atmosphere, some part of carbon is replaced by oxygen as can be seen in Fig. 2(c) and (d). Figure 2(a) shows that, in such a condition, the epitaxial layer retains a smooth surface. Since Er has a high tendency to form a complex with oxygen, we speculate that the changes in the light scattering intensity and the 4f luminescence spectrum are caused by the coupling of Er atoms with oxygen atoms on the growth surface.

We expect the appearance of many lines and broadening of each line as is seen in Fig. 1(a) for the luminescence from Er clusters, because there are various ways that the Er clusters can be

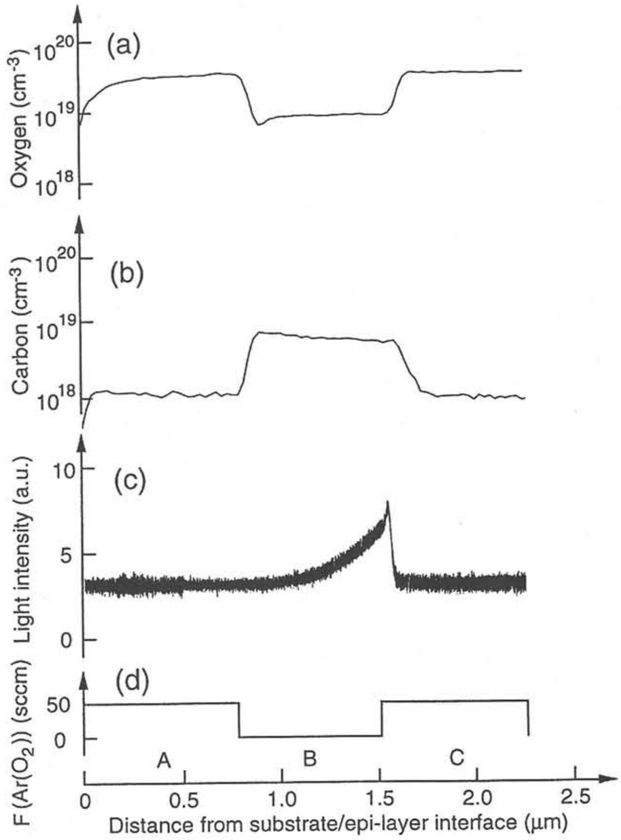

Fig. 2 The vertical axes show (a) oxygen and (b) carbon concentrations measured by SIMS, (c) the scattered light intensity from the surface, and (d) the flow rate of $Ar(O_2)$ gas into the reactor. The horizontal axis is the distance from the substrate/epi-layer interface. The horizontal axes for (c) and (d) were converted from the growth time using the growth rate of 1.45μm/h. The growth temperature is 550°C, and the Er concentration is 2×10^{19} cm^{-3}. The epitaxial layer is divided into three regions (*A* through *C*) according to changes in $Ar(O_2)$ gas flow rate.

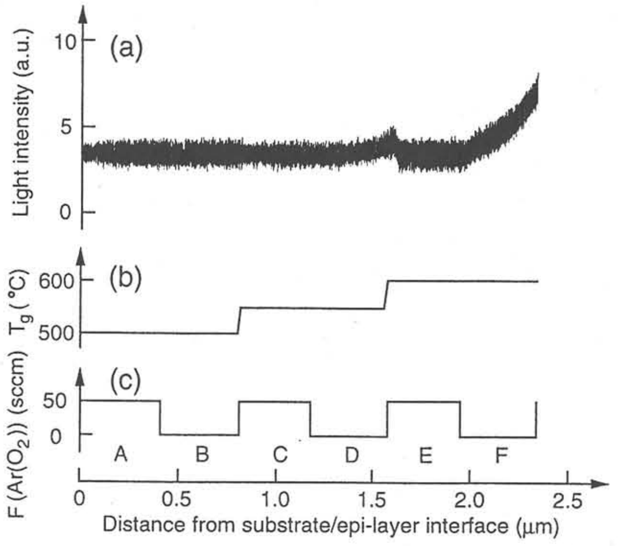

Fig. 3 The vertical axes are (a) the scattered light intensity, (b) the growth temperature, and (c) the flow rate of Ar(O_2) gas. The horizontal axis is the same as in Fig. 2. The Er concentration is 2×10^{19} cm^{-3}. The epitaxial layer is divided into six regions (*A* through *F*) according to changes in Ar(O_2) gas flow rate and growth temperature.

incorporated into the host. An dispersed Er center, on the other hand, is likely to take a specific atomic configuration in the host. When an Er atom migrates shorter distance before being incorporated into the GaAs host, it has a smaller chance of forming Er clusters. The experimental results indicate that the Er-O complex migrates shorter distance than other form of Er atoms on the growing surface. This must be due to either a lower mobility of the Er-O complex on the growing surface or a higher incorporation rate of the Er-O complex into the GaAs host.

Figure 3 shows additional evidence to support the speculation that the migration behavior of Er on the growth surface is related to the formation of Er clusters. In this growth experiment, the growth temperature was changed as well as the oxygen flow rate in the growth atmosphere. When the growth temperature is 500°C, the surface morphology is smooth regardless of oxygen content in the atmosphere, as seen in regions *A* and *B*. At the growth temperature of 550 and 600°C, however, the surface retains a smooth morphology only when oxygen is injected into the reactor, as seen in regions *C* through *F*. Without oxygen in the atmosphere, the surface becomes rough as the growth proceeds, and the rate of roughening is higher at a higher temperature, as can be seen by comparing regions *D* and *F*. We speculate that the rate of roughening is higher at a higher temperature because Er atoms migrate a longer distance at a higher growth temperature to form Er clusters. The formation of Er clusters is preferred because Er atoms in the form of clusters are thermodynamically more stable than unifromly dispersed Er atoms in GaAs host.

In the above discussion, it should be noted that the surface morphology during the growth does not show one to one correspondence to the type of PL spectrum. The PL spectra show many peaks or broad linewidths due to the presence of many types of Er centers in the sample grown at 500°C without oxygen and that grown at 600°C with oxygen, both of which have smooth surfaces. This is because the PL spectra reflect a microscopic surrounding atomic configuration around Er atoms such as formation of Er pairs, but the roughening of the grown surface becomes apparent only when Er atoms form larger clusters that disturb uniform growth of GaAs layers.

3. Conclusions

The intra-4f-shell luminescence spectra of Er^{3+} ion, the change in surface morphology during the epitaxial growth, and SIMS profiles of carbon and oxygen in the epitaxial layers suggest that optically active uniformly dispersed Er-oxygen complex is formed in GaAs by oxygen co-doping. This is explained as due to the preferential formation of the Er-oxygen complex center and the suppresion of Er-cluster formation on the growing surface.

Acknowledgements

The authors would like to thank Yoshiji Horikoshi and Kunihiko Uwai for stimulating discussions, and Tatsuya Kimura for continuous interest in this work.

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