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# Growth temperature dependence of the surface segregation of Er atoms in GaAs during molecular beam epitaxy

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We have quantitatively studied the temperature dependence of the surface segregation of Er atoms in GaAs during molecular beam epitaxy using secondary ion mass spectroscopy. It was found that a significant number of Er atoms segregate to the growing surface at temperatures of 400 °C and above and that the segregation decay length is approximately 0.5 μm at 500 °C, indicating that the incorporation ratio of Er atoms into GaAs is less than $10^{-3}$. In contrast to the growth at higher temperatures, GaAs overlayer growth at a temperature as low as 300 °C is effective in suppressing the surface segregation of Er and obtaining δ-doped structures. 

## 1. Introduction

Rare-earth-doped semiconductors have received much attention due to their characteristic emission of intra-4f-shell transitions. For example, Er-doped semiconductors are attractive because of their emission wavelength of around 1.5 μm, which corresponds to the optical communication wavelength range.[1)] Since the emission is due to the intra-4f shell transition from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) and the inner 4f shell is well shielded by the outer $(5s)^2$ and $(5p)^2$ electron shells, the wavelength is stable against changes in temperature[2)] and differences in the host semiconductor material.[3)] Thus, these luminescence properties are promising for fabricating light-emitting devices for optical fiber communication.[4)] Er-doped GaAs is often obtained by epitaxial growth, such as molecular beam epitaxy (MBE),[1,5,6)] metalorganic vapor phase epitaxy,[3,7,8)] and liquid phase epitaxy,[9)] along with ion implantation.[10,11)] The surface segregation of Er atoms during epitaxial growth is a significant obstacle to obtaining elaborate semiconductor structures.[12,13)] In particular, in order to fabricate Er δ-doped structures, which are expected to be applicable as single-photon sources in a similar way to N δ-doped GaP[14,15)] or N δ-doped GaAs,[16–20)] it is crucial to suppress the surface segregation of Er atoms during epitaxial growth. Although it is well known that Er atoms tend to segregate toward the surface during MBE growth,[12,13,21–23)] the surface segregation of Er atoms in GaAs has not yet been quantitatively investigated. In this study, we have grown Er δ-doped GaAs by MBE at various substrate temperatures for GaAs overlayer growth, and have quantitatively investigated the growth temperature dependence of the surface segregation of Er atoms during epitaxial growth by secondary ion mass spectrometry (SIMS).

## 2. Experimental procedure

The samples in this study were grown on undoped GaAs(001) substrates by solid-source MBE. Following the removal of the surface oxide at 610 °C, a 300-nm-thick GaAs buffer layer was grown at 580 °C. First, in order to investigate the temperature dependence of the sticking probability of Er atoms onto GaAs(001), Er δ doping was carried out at temperatures between 300 and 580 °C, and a 300 nm GaAs overlayer was grown at 300 °C, at which the surface segregation is well suppressed as mentioned later. The Er δ doping was performed for 1 min while the supply of Ga and As was interrupted.

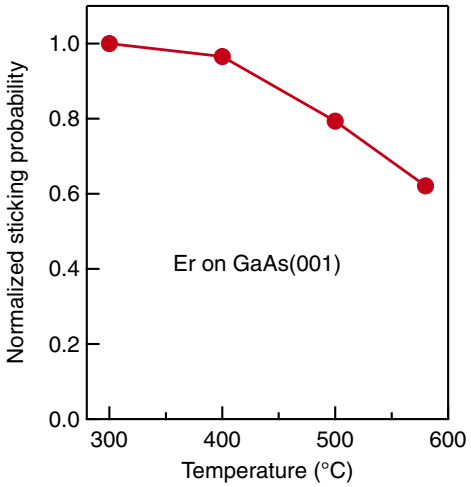


**Fig. 1.** (Color online) Normalized sticking probability of Er atoms on GaAs(001) surface.

Next, after Er δ doping at 300 °C for 1 min, a 300 nm GaAs overlayer was grown at 580, 500, 400, or 300 °C, and finally a thin GaAs cap layer was grown at 300 °C to study the temperature dependence of the surface segregation during MBE growth. The growth rate of GaAs was 0.1 nm/s and the As/Ga flux ratio was fixed at 10. The areal concentration of the Er δ doping was $4.6 \times 10^{10}$ cm$^{-2}$. The depth profile of the Er concentration was investigated by SIMS (CAMECA IMS-7f) using $O_2^+$ as the primary ion.

## 3. Results and discussion

### 3.1 Sticking probability

Figure 1 shows the temperature dependence of the normalized sticking probability of Er atoms on GaAs(001) obtained by the numerical integration of SIMS depth profiles of the Er concentration in GaAs grown at 300 °C after Er δ doping at different temperatures. In this figure, the sticking probability is normalized by that at 300 °C. The normalized sticking probability of Er atoms onto GaAs(001) decreases with increasing temperature and reaches approximately 60% at 580 °C, a typical temperature for GaAs MBE growth. Thus, we carried out Er δ doping at 300 °C in the following experiments to minimize the differences in the sticking probability of Er atoms.

 

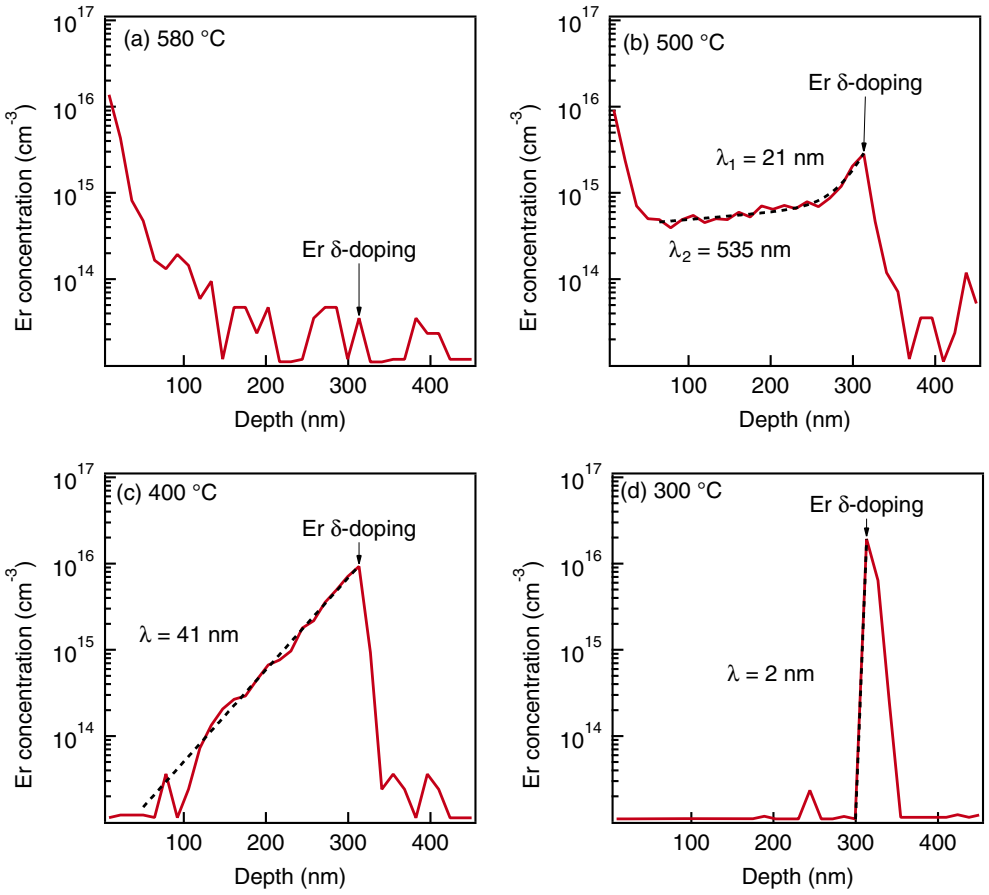


**Fig. 2.** (Color online) SIMS depth profiles of Er atoms in GaAs grown at various temperatures: (a) 580, (b) 500, (c) 400, and (d) 300 °C.

### 3.2 SIMS depth profile

Figures 2(a)–2(d) show the SIMS depth profiles of the Er concentration in GaAs overlayers grown at 580, 500, 400, and 300 °C, respectively, after Er $\delta$ doping at 300 °C. As shown in Fig. 2(a) (580 °C), no peak is observed at the Er $\delta$-doping position indicated by the arrow, while Er atoms are distributed near the surface. Since the total areal concentration of Er atoms was estimated to be $4.0 \times 10^{10}\,\mathrm{cm}^{-2}$ by integrating the SIMS depth profile of the Er concentration, only 13% of the supplied Er atoms were found to desorb with increasing temperature from 300 to 580 °C. Therefore, these results clearly show that most of the doped Er atoms segregate from the original Er $\delta$-doping position toward the surface during MBE growth at 580 °C.

In Fig. 2(b) (500 °C), a peak appears at the Er $\delta$-doping position. The Er concentration decreases rapidly at first and then gradually toward the surface, and Er atoms accumulate near the surface. The decay curve of Er concentration to the surface was fitted by two exponential terms; shorter and longer $1/e$ segregation decay lengths[24,25] of $\lambda_1 = 21$ nm and $\lambda_2 = 535$ nm were obtained, respectively. The fitted curve is shown as a dashed line in this figure. The nonexponential decay observed for the overlayer growth at 500 °C will be discussed later. These $1/e$ segregation decay lengths for Er atoms in GaAs are significantly longer than that for Ge atoms in Si[24] or In atoms in GaAs,[25] and comparable to that for Er atoms in Si.[21,22] The total areal concentration of Er atoms obtained by integration amounts to $4.6 \times 10^{10}\,\mathrm{cm}^{-2}$, showing that the desorption associated with the temperature increase from 300 to 500 °C is negligible. Since the areal concentration or Er atoms accumulated near the surface was calculated to be $2.2 \times 10^{10}\,\mathrm{cm}^{-2}$, about half of the Er atoms were found to segregate across the 300 nm GaAs overlayer.

For the GaAs overlayer growth at 400 °C, as shown in Fig. 2(c), the Er concentration exponentially decays from the $\delta$-doping position toward the surface. We obtained a $1/e$ segregation decay length of $\lambda = 41$ nm by fitting to the SIMS depth profile. The fitted curve is plotted as a dashed line in this figure. Unlike the overlayer growth at 500 and 580 °C, the accumulation of Er atoms is not observed near the surface at 400 °C, which indicates that the surface segregation of Er atoms is suppressed with decreasing temperature, and is thus kinetically limited.[24]

As shown in Fig. 2(d), a sharp peak appears at the $\delta$-doping position in the SIMS depth profile of the sample grown at 300 °C. In particular, the Er concentration decreases rapidly toward the surface. The $1/e$ segregation decay length was estimated to be 2 nm or less in spite of the detection limit of SIMS. The accumulation of Er atoms does not occur near the surface, similarly to in the overlayer growth at 400 °C. Thus, GaAs overlayer growth at a temperature as low as 300 °C is effective in suppressing the surface segregation of Er atoms, and in other words, Er $\delta$-doped structures are available only when the overlayer is grown at temperatures of 300 °C and below.

### 3.3 Segregation decay length

We show the temperature dependence of the $1/e$ segrega-

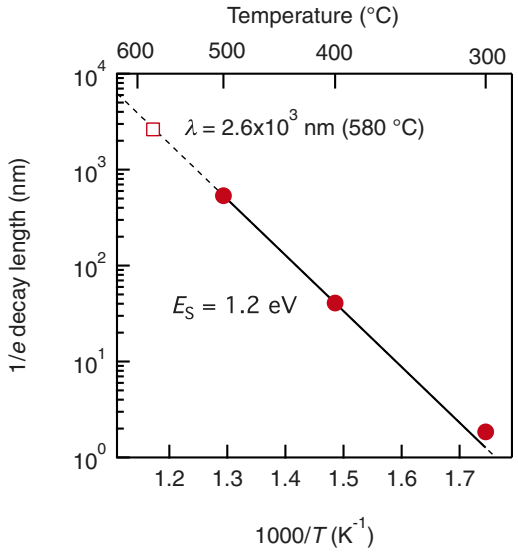


**Fig. 3.** (Color online) Temperature dependence of the $1/e$ segregation decay length of Er atoms in GaAs during MBE growth.

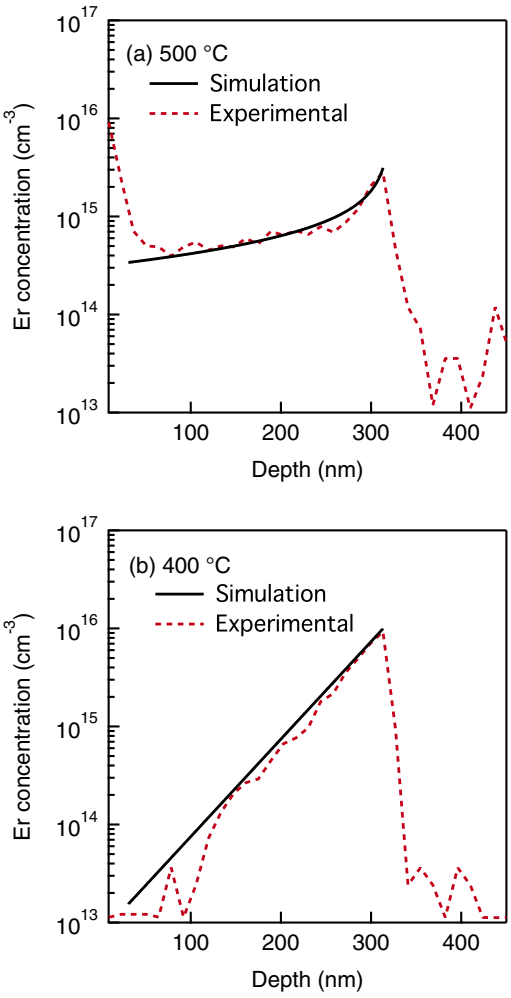


**Fig. 4.** (Color online) Simulated profiles of Er surface segregation grown at (a) 500 and (b) 400 °C.

tion decay length of Er atoms during GaAs MBE growth in Fig. 3. In this figure, only the longer decay length $\lambda_2$ is plotted for the overlayer growth at 500 °C. Assuming that the $1/e$ decay length follows the Arrhenius equation $\lambda \propto \exp(-E_S/k_BT)$ based on the surface diffusion model,[26] where $T$ is the absolute temperature, $k_B$ is the Boltzmann constant, and $E_S$ is the activation energy associated with surface diffusion, the temperature dependence of the decay length is well explained by the Arrhenius equation when $E_S = 1.2$ eV, as can be seen in the figure.

If the surface segregation is described by an exponential decay curve, the probability of surface segregation across one monolayer (ML) $R$ can be estimated from the segregation decay length $\lambda$ using the equation $R = \exp(-d/\lambda)$,[25] where $d$ is the thickness of one ML of [001]GaAs, i.e., half of the lattice constant. The segregation probability $R$ was calculated to be 87, 99.3, and 99.95% at 300, 400, and 500 °C, respectively, using the segregation decay length $\lambda$ obtained from the SIMS depth profiles. Therefore, the incorporation ratio $(1 - R)$ for Er atoms into GaAs is considerably small and was found to be 0.7 and 0.05% at 400 and 500 °C, respectively. In addition, the $1/e$ decay length at 580 °C was estimated to be $2.6 \times 10^3$ nm by extrapolating the Arrhenius equation, which leads to a segregation probability $R$ of 99.99%. Thus, only 0.01% of Er atoms are incorporated into GaAs at a typical MBE growth temperature. The Er concentration estimated from the incorporation ratio of 0.01% corresponds to $\sim 10^{14}$ cm$^{-3}$ in this study, which is in reasonable agreement with the fact that no peak is observed at the $\delta$-doping position for the GaAs overlayer growth at 580 °C.

### 3.4 Nonexponential decay

As mentioned previously, the Er concentration was observed to decay nonexponentially toward the surface for the GaAs overlayer grown at 500 °C as shown in Fig. 2(b). Such nonexponential decay has been reported for the surface segregation of Ge atoms in Si[24,27] and that of Sb atoms in Si,[28] and the mechanism has been attributed to self-limitation in the surface segregation. Thus, we simulated the experimental results at 500 and 400 °C based on a two-state exchange model taking self-limitation into consideration[24] by roughly choosing the rate at which atoms at subsurface sites jump to surface sites $p$, the rate at which atoms at surface sites return to subsurface sites $q$, and the initial concentration $n_0$. The simulated results are shown in Figs. 4(a) and 4(b). We set $p = 50$, $q = 0.01$, and $n_0 = 0.9$ for 500 °C, and $p = 0.9$, $q = 3 \times 10^{-4}$, and $n_0 = 7 \times 10^{-5}$ for 400 °C. Concerning $p$ and $q$, the values used for the simulation are close to the ones estimated from the Debye frequency of $10^{12}$–$10^{13}$ s$^{-1}$ and the kinetic barrier of 1.6–1.7 eV, and thus are plausible. In addition, $n_0$ at 400 °C was approximately set at the normalized initial concentration of $4.6 \times 10^{10}$ cm$^{-2}/6.3 \times 10^{14}$ cm$^{-2}$ (1 ML sheet concentration) $= 7.3 \times 10^{-5}$. However, we found that the nonexponential decay cannot be simulated without choosing a much larger $n_0$ at 500 °C than that at 400 °C. Since the actual initial concentration is $\sim 7 \times 10^{-5}$, $n_0 = 0.9$ means that $5 \times 10^{10}$ cm$^{-2} \simeq 10^{-4}$ ML becomes the effective saturation surface coverage for the surface segregation of Er atoms at 500 °C. Although the influence of surface steps is neglected for simplicity in the two-state exchange model[24] used for the simulation, surface segregation takes place as step hopping, and a segregating atom is incorporated when it is blocked at a step by another atom, as Nützel and Abstreiter suggested in the surface diffusion

model.[26] Furthermore, more than 90% of Er atoms are not incorporated and remain on the surface at 500 °C. Since the effective saturation surface coverage is determined by the step density if Er atoms are accumulated at steps, the Er concentration at which self-limitation occurs is likely to be considerably smaller than 1 ML for a flat GaAs surface with a terrace width >100 nm.[29] At 400 °C, the two-dimensional nuclear growth mode becomes dominant, and the step density, i.e., the effective saturated surface coverage, significantly increases. As a result, the low Er concentration used in this study is believed to lead to no self-limitation.

## 4. Conclusions

We quantitatively investigated the temperature dependence of the surface segregation of Er atoms during GaAs MBE growth using SIMS. A significant number of Er atoms were found to segregate to the growing surface at temperatures of 400 °C and above. The $1/e$ segregation decay lengths were 41 and 535 nm at 400 and 500 °C, which indicate that the incorporation ratios of Er atoms into GaAs are 0.7 and 0.05%, respectively. From the temperature dependence obtained in this study, the incorporation ratio was predicted to be 0.01% at a typical growth temperature of 580 °C. In contrast to the growth at temperatures of 400 °C and above, GaAs overlayer growth at a temperature as low as 300 °C is effective in suppressing the surface segregation of Er atoms, and in other words, Er $\delta$-doped structures are available only when the overlayer is grown at temperatures $\leq$300 °C.

## Acknowledgment

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