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Modeling and characterization of AlGaInAs and related materials using selective area growth by metal-organic vapor-phase epitaxy

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Abstract

Thicknesses and compositions of AlGaInAs-based layers grown by low-pressure metal-organic vapor-phase epitaxy (LP-MOVPE) in the regime of selective area growth (SAG) have been measured and calculated. In this study, we have grown InAs, GaAs and AlAs binary bulk layers on patterned InAs and GaAs substrates, respectively, in order to assess separately the vapor-phase diffusion (VPD) length (D/k) of indium, gallium and aluminum species. Special care has been taken in the evaluation of the Aluminum D/k ratio, on which little information was available. A 3D VPD model has been used to predict the composition and thickness profiles of various alloys. The calculated profiles have been compared to the experimental ones for GaInAs, AlInAs, AlGaInAs layers and GaAlAs layers deposited on patterned InP and GaAs substrates, respectively. The good agreement between modeling and experiment, together with the perfect selectivity obtained for all the different alloys, holds for the validity of the calculated D/k ratio of Al, Ga and In species. In MOVPE-SAG, the efficiency of a computational model is a key issue for the engineering of future SAG integrated optical devices. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The AlGaInAs active material system is considered as an alternative of considerable interest to the more conventional GaInAsP system for InP-based optoelectronic devices. This is mainly due to its larger conduction-band offset and smaller valence-band offset, leading to improved electrons confinement and hole density uniformity in quantum wells. Semiconductor optical devices commonly require the integration of at least one active section (laser, modulator, amplifier, etc.), with passive sections (low loss waveguide, filter, etc.). Therefore, the superior characteristics expected for AlGaInAs-based devices have generated a renewed interest for a well-known monolithic integration technique, namely selective area growth (SAG) [1–3], applied to AlGaInAs materials. In addition to specific difficulties of the SAG technique, it is certainly more complex to predict and control the diffusion variations of three III-elements (AlGaInAs) [4,5] rather than two (GaInAsP) [1,6–8] in the SAG regime. Therefore the SAG technique has been much more investigated for the GaInAsP system than for the AlGaInAs one.

In this work, we have investigated the whole {AlGaInAs} material family in the same SAG conditions in order to calculate the diffusion lengths D/k of the III elements, Al, Ga and In. Our simple 3D model based on vapor-phase diffusion (VPD), has been used to predict the composition and thickness variations for different cuts along the dielectric mask and it has also been compared to the experimental measurements.

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2. Experimental procedure

All {AlGaInAs} layers were grown by MOVPE in an AIX200/4 horizontal reactor designed for three 2-inch wafers [9,10]. Trimethylaluminum, trimethylgallium, trimethylindium, arsine and phosphine were the source materials. Purified hydrogen was used as a carrier gas. The growth conditions were optimized to achieve perfect selectivity, that is to avoid any polycrystalline deposition on the dielectric mask surface. The selectivity requirement is very important because any material deposited on the mask would be lost for the useful growth area and would lead to unpredictable layer compositions. The growth temperature was $650 \,^{\circ}$ C and the growth pressure was 150 mbar. The growth rate for the binary alloys was set at 0.1 nm/s.

The dielectric mask consisted of two 800 µm long SiO₂ stripes deposited on InP, InAs and GaAs substrates by chemical vapor deposition (CVD). The masked area width $(W_{\rm m})$ was varied from 20 to 160 µm while the open area width (W_0) between two mask stripes was varied from 20 to 60 µm. Each cell consisting of a combination of different $W_{\rm m}$ and $W_{\rm o}$, was separated from the nearest ones by 900 µm, which is far enough to consider no influence from one cell to another. The layer composition was evaluated from micro-photoluminescence (µPL) and X-ray diffraction (XRD) spectra. 3D thickness maps have been obtained using white light interferometric images. For some samples, secondary ion mass spectroscopy (SIMS) analysis has also been used to qualitatively compare the III element concentration variations. The SIMS analysis area was $30\,\mu\text{m}$ in diameter, in a $60 \times 60\,\mu\text{m}^2$ sputtered square, centered in the $W_0 = 60 \,\mu\text{m}$ open areas.

3. Modeling

In the SAG regime, the composition and thickness variations can be calculated using a model for the VPD of the different III-element species. This model was first introduced in the SAG regime by Gibbon et al. [1] for the GaInAsP material system. It assumes laminar flow, existence of a stagnant layer in contact with the wafer surface and no incorporation on mask surface (perfect selectivity). In the vapor phase, the molecules diffuse vertically and laterally, and nucleate on the exposed crystal surface. Surface diffusion is ignored in the present model as it occurs within a few µm of the dielectric. We calculated the concentration profiles by solving Laplace's equation with the following boundary conditions on the wafer (z = 0): $\partial N/\partial z = 0$ on the mask and $\partial N/\partial z = k/DN$ on the semiconductor, where $N (m^{-3})$ is the species concentration, z (m) is the vertical distance above the wafer, D (m^2/s) is the diffusion coefficient and k (m/s) is the reaction constant on the wafer. D/k is the effective diffusion length of the species under consideration. From the D/k values of the Al, Ga and In precursors, the VPD model yields the spatial distribution of the growth rate enhancement ratio (R) and the composition variations for the AlGaInAs layers grown in the SAG regime.

4. Results and discussion

We measured the thickness of various alloys of the AlGaInAs family grown in the SAG regime. The measurements at the center of the open area between two mask stripes were compared for each combination of $W_{\rm m}$ and W_{0} . All AlAs, InAs, GaAs binary, AlInAs, GaInAs, GaAlAs ternary and AlGaInAs quaternary layers were grown in the same growth conditions, on the appropriate InP, GaAs or InAs substrate. Growth temperature and AsH₃ flow were kept equal and constant in order to have the same V/III ratio for all the samples. InP layers only were necessarily grown under PH₃, but the measured thicknesses were found very similar to those of InAs layers. Growth rates were 0.1 nm/s for the binary alloys and up to 0.2 nm/s for all the other ternary or guaternary alloys. All the thickness profiles were normalized to the thickness measured in the field, far from the mask. Therefore, all the growth enhancement ratios (R) presented here are fully comparable. Fig. 1 shows, for $W_0 = 20 \,\mu\text{m}$ and different materials, the linear evolution of R as a function of $W_{\rm m}$. As usually reported, R(InAs) is much higher than R(GaAs). R(GaInAs) and R(AIInAs) values are found to be intermediate between those of R(InAs) and R(GaAs), which is compatible with the shortest diffusion length D/kattributed to In species. More surprisingly, $R(Ga_{0.41})$ $Al_{0.59}As$) is slightly higher than $R(Ga_{0.74}Al_{0.26}As)$, which itself is even higher than R(GaAs). This implies that in our growth conditions, aluminum has a shorter diffusion length than gallium. This is in contradiction with previous reports of a longer diffusion length for Al precursor than for Ga and In ones [4,11]. Fitting the experimental thickness profiles for InP, GaAs (Fig. 2) and GaAlAs (Fig. 3), allows to determine the D/k parameters. Diffusion lengths of In and Ga is about 10 and 85 µm, respectively. These values are in qualitative agreement with those



Fig. 1. *R* versus $W_{\rm m}$ for different {AlGaInAs} materials obtained in the same SAG conditions and for $W_{\rm o} = 20 \,\mu {\rm m}$.



Fig. 2. Cross-section normalized thickness profiles measured for InP and GaAs together with the calculated InP, AlAs and GaAs profiles.



Fig. 3. Cross-section normalized thickness profiles (measured and calculated) of a GaAlAs layer, by SAG.

reported in the literature [1,4,7,8]. Diffusion length of Al is 50 µm, intermediate between that of In and Ga. This implies that for the SAG of AlGaAs materials, the Al content will increase in the vicinity of the mask. In order to confirm this effect, SIMS measurements were performed near the SiO₂ mask stripes and compared to a reference, far from the mask. An increase of about 3% of aluminum was indeed found in the center of the open area ($W_0 = 60 \,\mu\text{m}$ and $W_{\rm m} = 230\,\mu{\rm m}$). This is not negligible since a longer diffusion length of aluminum species would have lead to an increase of several percents of the gallium content in the AlGaAs ternary alloy. The calculated D/k coefficients were used, without any further adjustment, to calculate the ternary and quaternary thickness and composition variations. In the case of AlInAs (Fig. 4), the agreement between simulation and experiment is quite remarkable.

Fig. 5 shows, on the left axis, the simulated composition variation in the stripe direction of a selectively grown AlGaInAs layer. The band gap wavelengths of the quaternary layer calculated from this composition varia-



Fig. 4. Cross-section normalized thickness profiles (measured and calculated) of an AlInAs layer, by SAG.



Fig. 5. AlGaInAs composition variation in the stripe direction (left axis) together with the corresponding measured (by μ PL) and calculated wavelength (right axis), obtained for $W_o = 20 \,\mu$ m, $W_m = 140 \,\mu$ m and a mask length of $300 \,\mu$ m.

tion and corrected with the strain are also reported on the right axis. The corresponding wavelengths measured by μ PL are in good agreement and validate the SAG modeling.

5. Summary and conclusions

We investigated the SAG of AlGaInAs by MOVPE. Different {AlGaInAs} binary, ternary and quaternary materials were grown selectively on SiO₂ patterned InAs, InP and GaAs substrates. Through the thickness measurements and using a model for the VPD of the Al, Ga and In species, the D/k diffusion lengths were calculated for the III elements (Al, Ga and In) and used to predict the AlGaInAs composition in the vicinity of the mask stripes. In our growth conditions, the aluminum D/k ratio was found intermediate between that of indium and gallium. Then, we have been able to evaluate the growth enhancement ratio R and the band gap shift for different mask patterns with a good agreement with the experimental measurements. Moreover, the high growth selectivity and the excellent control of the grown material composition indicate that the AlGaInAs SAG technique is well suited for the engineering of new photonic integrated devices.

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