Instability of partially disordered carbon-doped AlGaAs/GaAs superlattices

I. Szafranek, J. S. Major, Jr.,[a] B. T. Cunningham,[b] L. J. Guido,[c] N. Holonyak, Jr., and G. E. Stillman
Center for Compound Semiconductor Microelectronics, Materials Research Laboratory and Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Illinois 61801

(Received 20 July 1990; accepted for publication 1 October 1990)

Superlattices of $Al_{0.3}Ga_{0.7}As$/GaAs grown by metalorganic chemical vapor deposition and heavily doped with carbon using CCl_4 were annealed for 24 h at 825 °C under a variety of ambient and surface encapsulation conditions. Pronounced changes in photoluminescence from the annealed superlattices with storage time at room temperature, as opposed to an excellent reproducibility of that from the as-grown, not annealed samples, are reported. These changes may be indicative of degraded thermal stability of the annealed superlattice crystals due to high-temperature-induced lattice defects. The systematic failure to fabricate buried-heterostructure quantum well lasers via impurity-induced layer disordering in similarly doped AlGaAs/GaAs crystals, which may be related to the same effect, is also discussed.

High-temperature annealings have long been used to stimulate diffusion processes in quantum well heterostructures (QWHs) and superlattices (SLs) in attempts to modify the structure and thus the optical properties of the crystals (for a recent review on this subject, see Ref. 1). This procedure has been applied to both nominally undoped and doped crystals, the latter case being referred to as the impurity-induced layer disordering (IILD),[2] and it provides an important additional degree of freedom in device fabrication.[1] The layer intermixing effect is promoted by native defects whose concentrations increase at elevated temperatures. An important aspect of the potential applicability of the high-temperature heat treatments is the influence that such processes may have on the long-term stability of the optical and electrical properties of the annealed crystals.

In this letter we present an evidence of significant changes in luminescence properties of C-doped $Al_xGa_{1-x}As$/GaAs SL crystals during storage of several months at room temperature following annealing at 825 °C. This effect possibly indicates a structural instability of the annealed crystals due to high-temperature-induced lattice defects and, therefore, it may bear on performance of laser diodes and other electro-optical devices realized using IILD processing. Specifically, a systematic failure to fabricate buried-heterostructure QW lasers using IILD in similarly doped crystals is reported.

The crystals investigated here were grown by low-pressure metalorganic chemical vapor deposition (MOCVD) in an Emcore GS3100 reactor. The carbon doping source was a 500 ppm mixture of CCl_4 (Matheson) in high-purity H_2.[3,4] It provided an approximately uniform *p*-type doping level of $[C_{As}] \approx 8\times10^{18}$ cm^{-3} throughout the whole stack of GaAs and $Al_xGa_{1-x}As$ epitaxial layers, as determined by secondary-ion mass spectrometry (SIMS) and *C-V* electrochemical depth profiles. The growth conditions and the SL structure are described in detail elsewhere.[5]

The anneals were performed in evacuated quartz ampoules (volume ≈ 3 cm^3, $p \approx 10^{-6}$ Torr) at $T = 825$ °C for 24 h. Three sets of samples were annealed in separate ampoules with (i) an excess of elemental As – (+As), (ii) an excess of elemental Ga – (+Ga), and (iii) with neither Ga nor As added to the ampoule – (+0). A set of three samples was loaded into each ampoule: two were encapsulated with a CVD-grown ~1000-Å-thick layer of either SiO_2 or Si_3Ni_4, and the third sample was uncapped.

The optical properties of all the samples were assessed with low-temperature photoluminescence (PL). The samples were mounted strain-free in superfluid ^{4}He at $T \approx 1.7$ K, and were excited with the 5145 Å line from an AR^+ laser, using low power density of ~36 mW/cm^2. The emitted radiation was dispersed by an Instruments SA 1 m double spectrometer and detected by a thermoelectrically cooled GaAs photomultiplier tube, using the photon counting technique. The PL measurements were initially taken several weeks after the SL crystals were grown and annealed. Subsequently, all the samples (including the as-grown) were repeatedly measured under identical experimental conditions several times during a period of more than a year, while being stored at room temperature. An unfocused beam of about 3 mm in diameter was used to probe almost the entire area of the samples, thus averaging over possible lateral inhomogeneities of the crystals.

In the as-grown sample the SL-related low-temperature PL consists of a single, symmetric peak at $h\nu \approx 1.5316$ eV with full width at half maximum (FWHM) of ~17.6 meV. This peak is attributed to $n = 1$ electron-to-heavy hole ($e \rightarrow hh$) confined-particle recombination in GaAs QWs as discussed in detail elsewhere.[5] In the PL spectra of the annealed SLs this transition is accompanied

[a] Intel Doctoral Fellow.
[b] Now at Sandia National Laboratories, Division 1141, Albuquerque, NM 87185.
[c] Now at Yale University, Department of Electrical Engineering, Center for Microelectronic Materials and Structures, Box 2157 Yale Station, New Haven, CT 06520.

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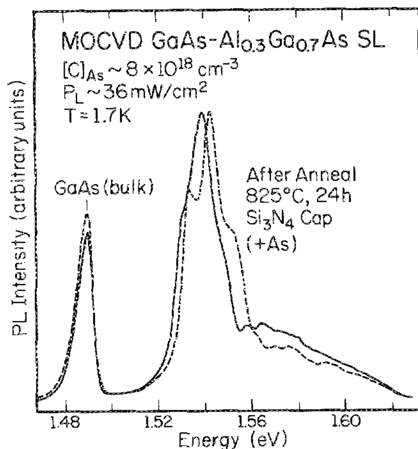

FIG. 1. Photoluminescence spectra of an annealed, heavily C-doped $Al_{0.3}Ga_{0.7}As/GaAs$ superlattice crystal, demonstrating the effect of instability of its optical properties as a function of storage time at room temperature. The solid-line spectrum was measured shortly after the sample was grown and annealed, and the dashed-line spectrum after several months of storage at room temperature.

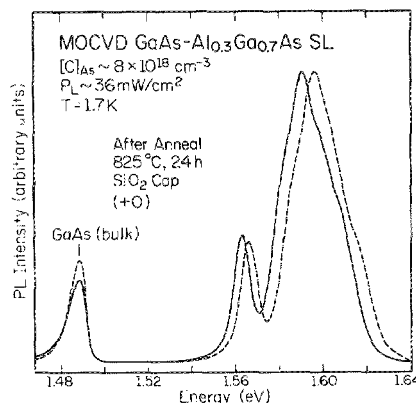

FIG. 2. Same as Fig. 1, but for different encapsulation and ambient conditions. A pronounced energy up-shift of the SL-related luminescence after a few months of room-temperature storage is evident, compared to a stable peak position of the bulk GaAs emission at ~1.488 eV. Variation in the relative PL intensity of the latter peak possibly indicates changes in electrical transport properties of the annealed SL crystals during storage at room temperature.

by shoulders and secondary peaks on both high- and low-energy sides (Figs. 1–3). The position of this SL-related luminescence is shifted to higher energies relative to that of the as-grown crystal, due to layer-disordering-induced grading of the alloy composition profile across the AlGaAs/GaAs heterointerfaces.[5] For the as-grown SL both the position and the line shape of the $(e\rightarrow \mathrm{hh})_{n=1}$ peak have remained practically unchanged during storage at room temperature. In contrast, virtually all the samples that underwent the post-growth, high-temperature anneals have exhibited clearly discernable variations in their PL spectra, with the extent and nature of these changes varying from sample to sample. It is the reproducibility of the energy and line shape of the SL-related luminescence during room-temperature storage that is of main concern in the present letter.

Three representative examples of the instability effect, covering various encapsulation and annealing ambient conditions, are shown in Figs. 1–3. Figure 1 presents two PL spectra measured at different times after the Si_3N_4-capped SL was annealed at (+ As) atmosphere. In this case, after a few months of storage at room temperature the $(e\rightarrow \mathrm{hh})_{n=1}$ peak position shifted up from 1.5396 to 1.5427 eV and the total line width increased from 20.1 to 24.5 meV. In additional PL measurements taken on this sample, both the position and the linewidth of this peak have continued to fluctuate. The low-energy transition at ~1.488 eV, visible in Figs. 1–3, is assigned to unresolved conduction band-to-acceptor (e–A^0) and donor-to-acceptor (D^0–A^0) recombination processes due to C_{As} acceptors in the bulk GaAs, namely, the buffer layer and the substrate.[5] The peak position of this transition is invariant with both annealing, and the subsequent storage of the annealed samples at room temperature. These observations indicate that the spectral modifications are limited to the AlGaAs/GaAs multilayer stack. Therefore the instability of the optical properties may be related to long-term structural changes taking place in the annealed SL crystals, presumably due to high-temperature-induced lattice defects.

Another example of SL instability is shown in Fig. 2 for the SiO_2-capped sample annealed under (+ 0) conditions. In this case the line shape changes of the SL-related luminescence are less pronounced, and the main effect is a significant energy up-shift of the dominant SL peak from 1.5905 to 1.5967 eV with respect to the stable emission line of the bulk GaAs at ~1.488 eV. As in Fig. 1, the relative PL intensity of the latter peak increased slightly with storage time. Similar PL intensity changes have been observed for almost all of the annealed samples, alongside modifications of the SL-related luminescence. The observation of occasionally very intense bulk GaAs luminescence through the ~1-μm-thick SL stack indicates a large ambipolar diffusion length of the photogenerated carriers and/or a photon recycling effect.[6] Therefore, the varying intensity of this deep emission may be indicative of changing carrier transport properties of the annealed SLs with storage time providing additional support of the SL instability argument.

The room-temperature instability of the capless SL annealed under (+ Ga) ambient is shown in Fig. 3. After a few months of storage the SL-related luminescence transformed from a broad doublet at 1.5590–1.5693 eV (the solid-line spectrum) into a narrower single peak at 1.554 eV (the dashed curve in Fig. 3). Such a down-shift in PL energy roles out an ongoing process of post-anneal interface disordering as a possible interpretation of the PL changes with time. In this sample and a few others, an intense PL peak on the low-energy side of the bulk GaAs band has been detected. For the SL in Fig. 3 this peak has shifted from 1.4758 to 1.4686 eV and the FWHM increased from 11.9 to 15.5 meV. The exact origin of this peak is not known, but the facts that the PL energy and line shape become significantly modified, as opposed to the stable bulk GaAs line at ~1.49 eV, seem to imply that this transition is SL related. With increasing sample tempera-

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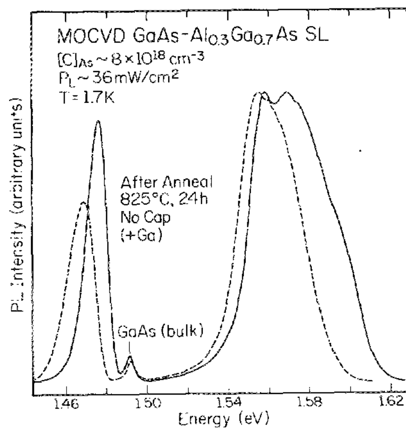

FIG. 3. Same as Figs. 1 and 2, but for different surface encapsulation and annealing ambient conditions. The shift to lower energy of the $(e \rightarrow hh)_{n=1}$ transition in the dashed spectrum precludes a continuing process of layer disordering during storage at room temperature as a possible explanation of the instability effect.

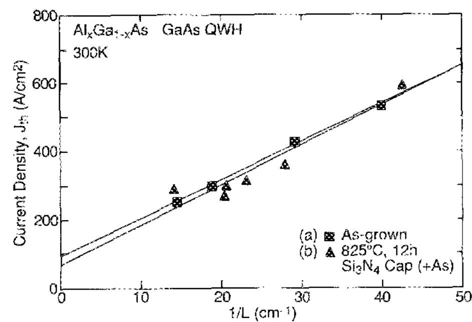

FIG. 4. Threshold current density (J_{th}, A/cm^2) vs reciprocal length ($1/L$, cm^{-1}) for broad-area diodes fabricated from both (a) as-grown and (b) annealed C-doped (CCl_{n4}) QWH laser diode material. The gain parameter β has values of 0.090 and 0.085 cm/A for as-grown and annealed C-doped QWH material, respectively. The distributed loss parameter α has also decreased during the anneal from an as-grown value of 8.33 cm^{-1} to an annealed value of 5.53 cm^{-1}. Following the anneal, the general lasing characteristics of the material remain acceptable.

ture in the 1.7–21 K range this peak quenches rapidly, while both shifting and broadening toward lower energy, opposite of the behavior expected from $(e\text{–}A^0)$ and $(D^0\text{–}A^0)$ recombination processes in bulk material.

Within the limited data available, the most stable annealed SL structures have been those that underwent the most extensive layer intermixing during the thermal treatments, namely, the capless and SiO_2-capped crystals annealed under (+ As) ambient.[5] In both cases there was practically no line shape modification and the $(e \rightarrow hh)_{n=1}$ peak position shifted by less than 2 meV. This result may suggest that the latent potential for further structural changes after annealing is relatively reduced when significant Al, Ga, and native defect self-diffusion takes place during the high-temperature processing.

Anomalous behavior has also been observed in Si-IILD buried-heterostructure laser diodes fabricated from $Al_xGa_{1-x}As/GaAs$ and $Al_yGa_{1-y}As/GaAs/In_xGa_{1-x}As$ QWH laser material employing C (from CCl_4) as the p-type dopant. Figure 4 shows the curves of threshold current density (J_{th}, A/cm^2) versus reciprocal length ($1/L$, cm^{-1}) for broad-area diodes fabricated from both as-grown [Fig. 4(a)] and annealed [Fig. 4(b)] C-doped (CCl_4) QWH laser diode material. The anneal procedure employed here is 12 h at 825 °C under As overpressure. For the anneal cycle the sample is encapsulated with CVD Si_3N_4. After the anneal the calculated distributed gain and loss parameters, β and α, respectively, have both decreased slightly, although the overall performance of the QWH laser diode material following the anneal cycle is still quite acceptable. The parameters β and α have been calculated using[7]

$$J_{th} = \alpha/\beta - [\ln(R_1R_2)]/(2\beta L).$$

where L is the laser diode bar length and R_1 and R_2 are the mirror reflectances. Since these anneal conditions are similar to those used in the fabrication of index-guided laser diodes via Si-IILD, C-doped (CCl_4) QWH laser diode structures should be excellent candidates for Si-IILD procedures. However, to date we have been unable to fabricate Si-IILD diodes from a large variety of either $Al_xGa_{1-x}As/GaAs$ or strained-layer $Al_yGa_{1-y}As/GaAs/In_xGa_{1-x}As$ QWH laser crystals employing C from CCl_4 as the p-type dopant. Although these data are as yet unexplained, it should be noted that Si-IILD laser diodes operating cw at 300 K up to a current of $I = 7I_{th}$, where $I_{th} \approx 25$ mA is the average threshold current, have been fabricated from structures grown at high temperatures (760–825 °C) in the same Emcore rector used in this work but employing C from TMGa as the p-type dopant.[8] Therefore it is conceivable that the anomalous behavior of the crystals doped with C from CCl_4, grown at lower temperatures, is related to increased O_2 concentrations in AlGaAs layers and/or other growth-induced effects specific to C doping with the CCl_4 source.

The technical assistance of M. K. Suits, R. MacFarlane, and R. T. Gladin in preparation of this manuscript is appreciated. This work has been supported by the Joint Services Electronics Program, under contract N00015-84-C-0149, by the National Science Foundation, under grants DMR 86-12860 and CDR 85-22666, and by SDIO/IST under contact No. DAAL 03-89-K-0080 administered by the Army Research Office.

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