sharply defined, and its TED pattern is a typical reciprocal plane {111}. The TED pattern was conserved over at least a $130 \times 130 \mu m^2$ sample area and no extra spot appeared. This confirms the achievement of a $130 \times 130 \mu m^2$ single crystal film by means of the method being discussed here.

Figure 2(b) shows that each corner of the rhomboidal patterns is rounded. The corresponding TED pattern consists of a pair of hexagonal spots on the (220) diffraction ring, and irregular spots on the (311) diffraction ring. This signifies that this part of the sample is a polycrystal including weak {111} twin texture. All ring patterns in Figs. 2(a) and 2(b) are assigned as being from gold.

The crystal orientation within the substrate surface plane is shown in Fig. 3, where the angular relationship between the TEM photograph and TED pattern is depicted. The relationship was confirmed by observing the TEM and TED patterns for a MoO_2 crystal in the same equipment. The two crystal ⟨110⟩ axes are normal to the rhomboid sides. This relationship is roughly conserved even in the incomplete film shown in Fig. 2(b). It is thus deduced that the crystal axis is aligned by the rhomboidal Au pattern.

In conclusion, a new method for growing crystals on an amorphous substrate, in which a patterned metal film aligns with the crystal axis, was reported. The Au film used as the metal was patterned into a rhomboidal shape with 60° and 120° apex angles. A silicon crystal with a $130 \times 130 \mu m^2$ area was grown on a fused quartz substrate, with ⟨111⟩ normal to the substrate, an ⟨110⟩ normal to each side of the Au rhomboid.

The crystal growth process employing controlled precipitation from a Si-Au supersaturated solution will be applicable to semiconductor materials other than Si, such as Ge, GaAs,[9] GaP,[10] and GaAsP.[11] Growth temperature was also very low. This process will be compatible with the integration of several kinds of materials on an identical substrate.

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[1]M. W. Geis, D. C. Flanders, and H. I. Smith, Appl. Phys. Lett. **35**, 71 (1979).
[2]M. Tamura, H. Tamura, and T. Tokuyama, Jpn. J. Appl. Phys. **19**, L23 (1980).
[3]H. Mori, Jpn. J. Appl. Phys. **12**, L905 (1981).
[4]E. I. Givargizov, N. N. Sheftal, and V. I. Klykov, Proc. 5th Int. Conf. of Vapor Growth & Epitaxy 1981, p. 195.
[5]R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).
[6]M. Hatzakis, B. J. Canavello, and J. M. Shaw, IBM J. Res. Develop. **24**, 452 (1980).
[7]This step is not always needed for crystal growth. In recent experiment, crystal can be grown by only patterned gold film of 100-nm thickness.
[8]K. Ishiwatari, T. Oka, and K. Akiyama, Jpn. J. Appl. Phys. **6**, 1170 (1967).
[9]R. L. Barns and W. C. Ellis, J. Appl. Phys. **7**, 2296 (1965).
[10]N. Holonyak Jr., C. M. Wolfe, and J. S. Moore, Appl. Phys. Lett. **6**, 64 (1965).
[11]C. M. Wolfe, C. J. Nuese, and N. Holonyak Jr., J. Appl. Phys. **36**, 3790 (1965).

Improved photoluminescence of organometallic vapor phase epitaxial AlGaAs using a new gettering technique on the arsine source

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Using an aluminum-gallium-indium ternary melt for the removal of oxygen and moisture from the arsine source, substantial improvement in the quality of organometallic vapor phase epitaxial AlGaAs can be achieved. The arsine is bubbled through the ternary melt at room temperature prior to its introduction into a low-pressure reactor. Low-temperature photoluminescence spectra indicate an improvement in the sharpness of the bound exciton transition after the use of this gettering technique.

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The growth of AlGaAs by organometallic vapor phase epitaxy (OMVPE) requires oxygen and moisture-free growth ambients to avoid compensation by an oxygen-related deep luminescence center.[1] The major source of moisture appears to have its origin in the arsine source. Methods of gettering previously used to improve the optical film quality include the use of a molecular sieve on the arsine, incorporation of graphite baffles in the reaction cell,[2] and the growth of epitaxial buffer layers containing aluminum.[3]

In an earlier letter[4] we reported the use of the Al-Ga-In ternary melt for the removal of large quantities of moisture from hydrogen and nitrogen. Similar results were expected for the purification of arsine, but direct evidence of reducing oxygen and moisture from this gas was not obtained in the previous apparatus. In this letter we report the effects on the low-temperature photoluminescence spectra of

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$Al_xGa_{1-x}As$ ($x \sim 0.25$) films grown in a low-pressure OMVPE apparatus with the arsine source bubbled through the metallic melt.The results indicate an improvement in the epitaxial layer quality, which demonstrates the effectiveness of this method in gettering moisture and/or oxygen from arsine.

The arsine gas[5] used in the experiments was taken from a concentrated liquid source. The Al-Ga-In melt was prepared by the procedure described in an earlier publication.[4] Films were grown at 76 Torr with trimethylgallium and trimethylaluminum sources. The substrate temperature and V/III mole ratios used in the experiments were in the range of 700–800 °C and 20–60, respectively. All films were unintentially doped.

The film characterization was accomplished using low-temperature (3 K) photoluminescence (PL) data. The excitation wavelength and intensity for the PL measurements were 4825 Å and 100 mw/cm^2, respectively. The residual acceptors were identified from the PL spectra from the work of Stringfellow and Linnebach[6] and Mircea-Roussel *et al.*,[7] and the composition of the AlGaAs was obtained from calibrations obtained by Dingle *et al.*[8] The bound exciton transition was identified by observing the relative change of PL intensity with excitation intensity.[9] Additional PL experiments at longer wavelengths produced no observable luminescence due to oxygen-related deep centers. In addition, the background carrier concentration was evaluated using *C-V* measurements.

The effects on treating arsine with the ternary melt are most pronounced at lower growth temperatures. For example, PL spectra are shown in Fig. 1 for $Al_{0.26}Ga_{0.74}As$ layers grown with and without the melt at 700 °C at a V/III ratio of 40. This illustrates that the PL efficiency of the bound exciton (BE) is improved by a factor in excess of 5, and its half-width is reduced to less than 5 meV after the use of this gettering technique. The sharpness of this PL spectrum represents an improvement in the state of the art for OMVPE AlGaAs of this alloy composition. The background electron concentration of these films grown at 700 °C was approximately 1×10^{15} cm^{-3}. At higher substrate temperature, e.g., 800 °C, the bound exciton PL efficiency is increased slightly by treating the arsine, but this occurs at the expense of greatly increased carbon incorporation in the film. Carbon is the dominant acceptor as seen in Figs. 1 and 2 for films grown at 700 and 800 °C. However, small zinc concentrations were evident when the spectra were taken at higher excitation intensities.

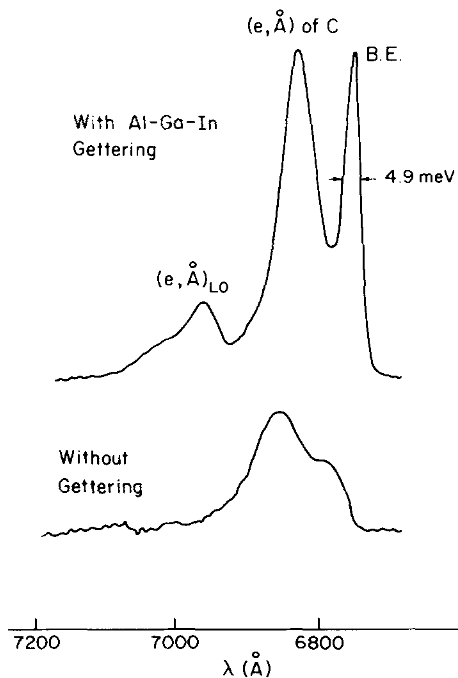

FIG. 1. Comparison of 3-K PL spectra for $Al_{0.26}Ga_{0.74}As$ films grown at 700 °C and V/III = 40 with and without Al-Ga-In gettering. (The vertical scale is arbitrary and has a shifted zero.)

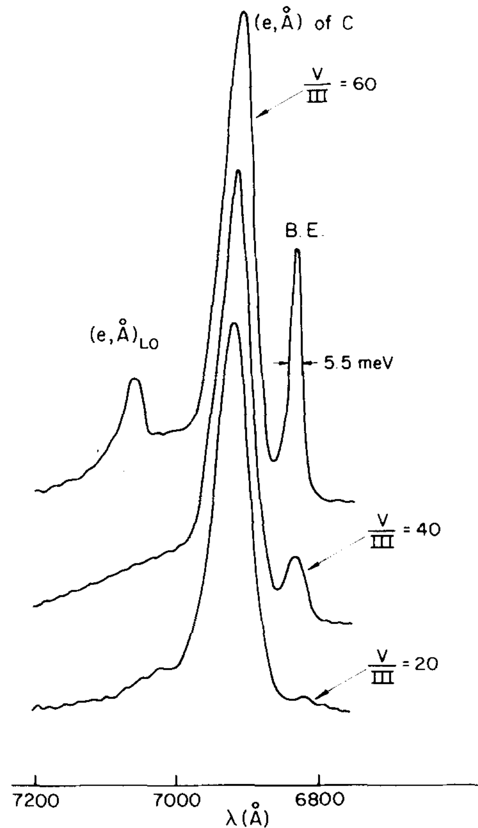

FIG. 2. Comparison of 3-K PL spectra for $Al_{0.24}Ga_{0.76}As$ films grown at 800 °C with Al-Ga-In gettering for various V/III ratios. (The vertical scale is arbitrary and has shifted zeroes.)

At a given substrate temperature, the bound exciton PL efficiency increases by over an order of magnitude with increased V/III ratio. This is illustrated in Fig. 2 for $Al_{0.24}Ga_{0.76}As$ layers grown at 800 °C using the gettering technique. Further improvements in the bound excition structure would be expected if higher V/III ratios could be used. Nevertheless, we find that the best linewidths and PL efficiency of the bound excition are obtained at lower growth temperatures near 700 °C when the gettering technique is used. Not only is carbon incorporation greatly reduced at this temperature, but the net carrier concentration is also lower (1×10^{15} cm^{-3}). Films grown at 800 °C have electron concentrations of about 5×10^{16} cm^{-3} when gettering is used. When gettering is not used this value drops to about 1×10^{16} cm^{-3}, indicating increased compensation by oxy-

gen-related deep centers.

In conclusion, we have demonstrated that by applying a new gettering technique for the removal of oxygen and moisture from the arsine, epitaxial layers of AlGaAs grown by OMVPE have improved the photoluminescence efficiency. The Al-Ga-In melt has a large capacity for the purification of arsine when excess solid aluminum is added to the melt. The best quality AlGaAs films are reproducibly obtained at low growth temperatures ($\sim$700 °C) and high V/III ratios when the arsine is treated by this technique.

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[1]M. J. Tsai, M. M. Tashima, B. L. Twu, and R. L. Moon, presented at the GaAs and Related Compounds Symposium, Albuquerque, NM, Sept. 1982.
[2]D. W. Kisker and J. N. Miller, Appl. Phys. Lett. **40**, 614 (1982).
[3]S. D. Hersee, M. A. DiForte-Poisson, M. Baldy, and J. P. Duchemin, J. Cryst. Growth **55**, 53 (1981).
[4]J. R. Shealy and J. M. Woodall, Appl. Phys. Lett. **41**, 88 (1982).
[5]5N Electronic grade obtained from Phoenix Research, LaMesa, CA.
[6]G. B. Stringfellow and R. Linnebach, J. Appl. Phys. **51**, 2212 (1980).
[7]A. Mircea-Roussel, A. Briere, and J. Hallasi, J. Appl. Phys. **53**, 4351 (1982).
[8]R. Dingle, R. A. Logan, and J. R. Arthur, Jr., Inst. Phys. Conf. Ser. **33a**, 210 (1977).
[9]G. Wicks, W. I. Wang, C. E. C. Wood, L. F. Eastman, and L. Rathbun, J. Appl. Phys. **52**, 5792 (1981).

Surface chemical reactions on $In_{0.53}Ga_{0.47}As$

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Dark currents on $In_{0.53}Ga_{0.47}As$ mesa photodiodes can be reduced significantly by treating the surfaces with H_2SO_4:H_2O_2:$X\,H_2O$ ($10 \leqslant X \leqslant 500$) instead of the usual bromine-methanol etch. Using spectroscopic ellipsometry we show that peroxide etches form porous amorphous As or oxide overlayers according to whether the *p*H values are less than or greater than ~ 3. The identity of these overlayers is established by their dielectric response and chemical reactivity.

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The magnitude of reverse leakage ("dark") currents of $In_{0.53}Ga_{0.47}As$/InP *p-n* junction photodiodes is of crucial importance in determining their performance as photodetectors in fiberoptic receivers.[1] In an empirical study of the effect of surface treatments on mesa diodes, we discovered that 1:1:X (H_2SO_4:H_2O_2:$X\,H_2O$) etchants substantially reduced dark currents as compared to bromine-methanol (BrM) etchants. In addition, diodes etched in 1:1:X were more stable over extended periods of time than BrM-etched diodes.

Photodetectors are made by diffusing Zn at 500–550 °C (Ref. 2) to a depth of 1.5–3 μm into 4–7-μm-thick layers of nominally undoped ($2\text{–}6\times 10^{15}$ cm^{-3}) *n*-type $In_{0.53}Ga_{0.47}As$ grown via liquid phase epitaxy (LPE) on (100) InP:Sn or InP:S substrates. Ohmic contacts were then formed by alloying evaporated or electroplated Au-Zn and Au-Sn films at $T = 400$ °C for 10 s. Photolithographically defined mesas were then etched with either 1% BrM or 1:1:10 (H_2SO_4-:H_2O_2:H_2O). In one instance, grown *p-n* junctions were investigated with similar results.

Figure 1 illustrates the dramatic reduction of the reverse leakage current (dark current) of mesa diode attainable by etching with 1:1:X. The dark current of a 6×10^{-5} cm^{-2} diode at -10 V is reduced from the 10-nA value obtained with BrM to 1 nA after 20 s in 1:1:50. Because the capacitance changed only from 0.39 to 0.37 pf, we can conclude that the mesa area has been reduced by no more than 6% by the re-etching procedure. This is confirmed by direct visual inspection and is also consistent with the etch rate of $\sim$2200 Å/min for 1:1:50. The effectiveness of the 1:1:X etch in reducing leakage current has been established with data taken on several hundred diodes, both on the wafers and after bonding.

These empirical results motivated us to a study of the effect of these etches on large area (3×3 mm^2) $\langle 100\rangle$ surfaces of $In_{0.53}Ga_{0.47}As$. Our approach is spectroscopic ellipsometry, where the apparent or pseudodielectric function $\langle\epsilon\rangle = \langle\epsilon_1\rangle + i\langle\epsilon_2\rangle$ is measured at the E_2 peak at 4.50 eV of the ϵ_2 spectrum of the substrate material as a function of surface treatment.[3,4] The $\langle\epsilon\rangle$ values provide a sensitive and unambiguous indication of surface quality and of the presence or absence of films in the thickness range below 100 Å.[4,5] We also use this method to obtain information about the compositions of films by studying their resistance to attack by selected chemical reagents and compare the results with the known solubilities[6–8] of the oxides and metals under consideration. Instrumentation and techniques have been described in detail elsewhere.[4,9]

The results of various chemical treatments are shown as

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