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Metalorganic vapor-phase epitaxy of III/V phosphides with tertiarybutylphosphine and tertiarybutylarsine

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Abstract

Indium phosphide, gallium arsenide phosphide, and aluminum indium phosphide have been deposited by metalorganic vapor-phase epitaxy using tertiarybutylphosphine and tertiarybutylarsine. The effects of growth temperature and V/III ratio on the amount of silicon, sulfur, carbon, and oxygen in InP have been determined. Minimum incorporation was observed at 565 °C and a V/III ratio of 32. In this case, the material contained a background carrier concentration of $2.7 \times 10^{14}\,cm^{-3}$, and the Hall mobilities were 4970 and 135,000 $cm^2/V\,s$ at 300 and 77 K. The oxygen contamination in AlInP was found to be only $9.0 \times 10^{15}\,cm^{-3}$ for deposition at 650 °C and a V/III ratio of 35. The relative distribution of arsenic to phosphorus in $GaAs_yP_{1-y}$ was determined at temperatures between 525 and 575 °C. The distribution coefficient $[(N_{As}/N_P)_{film}/(P_{TBAs}/P_{TBP})_{gas}]$ ranged from 25.4 to 8.4, and exhibited an Arrhenius relationship with an apparent activation energy of 1.2 eV.
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1. Introduction

Metalorganic vapor-phase epitaxy (MOVPE) is a crucial technology for compound semiconductor device manufacturing. Compared to

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molecular beam epitaxy (MBE), the other widely adopted growth process, MOVPE has the advantage of somewhat greater flexibility in materials composition, especially for alloys containing phosphorus [1]. However, MOVPE reactors consume large quantities of hazardous chemical precursors. In particular, the conventional group V precursors, arsine and phosphine, have lethal doses (LC_{50}) well below 50 ppm [1–4]. This puts stringent demands on the safety equipment, and adds to the production costs.

Tertiarybutylphosphine (TBP) and tertiarybutylarsine (TBAs) have been shown to be suitable alternatives to arsine and phosphine. These precursors are less toxic ($LC_{50} = 70$ ppm for TBAs, and > 1100 ppm for TBP), and decompose upon air exposure to form relatively harmless solid oxides [1–4]. Liquid TBP and TBAs can be stored in bubblers at room temperature and mounted directly onto the MOVPE system. This reduces the danger to workers, as liquid materials disperse at rates several orders of magnitude slower than gases [3]. In addition, these precursors exhibit higher incorporation efficiencies than the hydrides, so that growth can be carried out at lower V/III ratios and substrate temperatures.

One of the main obstacles to the use of TBP and TBAs has been the presence of oxygen impurities in AlInP and AlInGaP at levels equal to or above $10^{17}\,cm^{-3}$ [5–10]. Nevertheless, recent advancements in precursor purification may have overcome these drawbacks, suggesting that it is worthwhile to reexamine these sources for III/V MOVPE. In this work, we have investigated the growth of InP, AlInP and GaAsP using tertiarybutylphosphine and tertiarybutylarsine. It was found that impurity concentrations below mid-$10^{14}\,cm^{-3}$ for InP and $10^{16}\,cm^{-3}$ for AlInP could be achieved at relatively low process temperatures and V/III ratios. In addition, the As/P segregation curves have been determined for GaAsP deposition between 525 and 575 °C. As expected, significantly lower arsenic distribution coefficients were obtained with TBAs and TBP as compared to those reported for alloy growth with the hydrides.

2. Experimental methods

The compound semiconductor films were grown in a Veeco (formerly Emcore) Discovery-125 MOVPE system, equipped with a sample loadlock having a base pressure of 1×10^{-7} Torr. The reactor was fed with UHP grade hydrogen that was further treated with a SAES Pure Gas, Inc. purifier (Model PS4 Series) to remove any remaining oxygen, nitrogen or carbon species to below one part per billion. The metalorganic precursors were trimethylgallium (TMGa), solution trimethylindium (TMIn), tertiarybutylphosphine (TBP), and tertiarybutylarsine (TBAs) from Epichem, Inc. Gallium arsenide phosphide and aluminum indium phosphide were deposited on 2″ GaAs (0 0 1) wafers, while indium phosphide was grown on InP (0 0 1) wafers. The substrate miscut angles were less than 0.3° towards the (1 1 0) plane. The growth rates and substrate temperatures were monitored in real time by an emissivity-corrected pyrometer (Veeco RealTemp™).

The InP films were deposited at 520, 565, and 610 °C, and V/III ratios varying from 10 to 32. The TMIn flow was kept constant during the run at 2.4 mTorr, which yielded a growth rate of 3.4 ± 0.1 Å/s. Lattice-matched AlInP on GaAs was deposited at 600 and 650 °C with V/III ratios of 35 and 65, respectively. The partial pressures of the group III sources ranged from 1.8 to 4.4 mTorr in these runs, yielding growth rates between 2.5 and 6.3 ± 0.2 Å/s. All runs were carried out at a total pressure of 60 Torr. Each day prior to the first run, the sample platter and reactor were baked for 0.5 h in flowing hydrogen at 750 °C. In addition, they were coated with a $\frac{1}{4}$-μm-thick layer of the base III/V material, if the substrate was different from the previous run.

After growth, the compound semiconductor films were characterized by high-resolution X-ray diffraction (HRXRD), photoluminescence spectroscopy (PL), secondary ion mass spectroscopy (SIMS), and Hall measurements. The XRD spectra were recorded on a Bede D^3 instrument at UCLA. The PL maps were provided courtesy of Veeco, Inc. The SIMS work was performed at Charles Evans & Associates, Inc., while Dr. Han

at Microlink Devices, Inc., made the Hall measurements.

3. Results and discussion

3.1. Indium phosphide

In Figs. 1–3 SIMS profiles are shown for InP films grown using TMIn and TBP. The substrate temperature and V/III ratio used to produce each layer in the film are listed in Table 1. Note that a lattice-matched InGaAsP layer ($\lambda = 1.3\,\mu m$) was inserted in between the film and the buffer layer so that growth rates could be monitored by reflectometry. The impurities monitored by SIMS were oxygen, carbon, sulfur, and silicon. No oxygen was detected in any of the layers, indicating that the concentration of this species was below $7.5 \times 10^{15}\,cm^{-3}$.

A comparison of layers 1, 3 and 4 in Fig. 1 reveals that the carbon concentration decreases slightly with increasing temperature. At a V/III ratio of 32, the carbon doping level equals $4.7 \times 10^{15}\,cm^{-3}$ at 610 °C and $1.0 \times 10^{16}\,cm^{-3}$ at 520 °C. On the other hand, the carbon concentration is not significantly affected by the V/III ratio, at least for values between 10 (layers 5 and 6) and 32 (layers 3 and 4). The rapidly increasing carbon level seen in layer 7 is probably due to an artifact of the SIMS analysis.

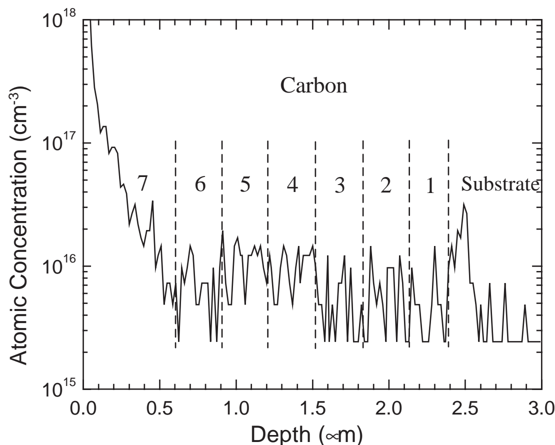

Fig. 1. SIMS profile for carbon in indium phosphide. Growth conditions are listed in Table 1.

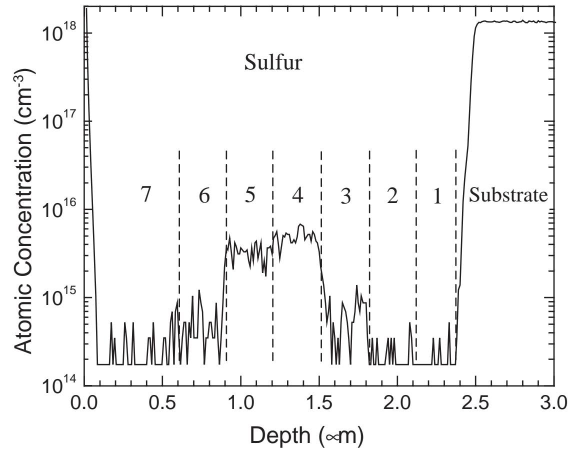

Fig. 2. SIMS profile of sulfur in indium phosphide. Growth conditions are listed in Table 1.

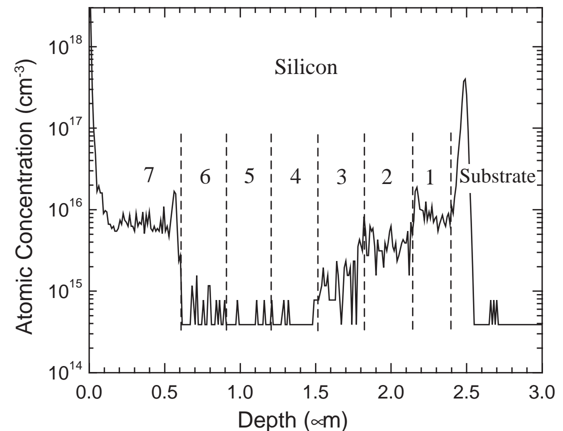

Fig. 3. SIMS profile of silicon in indium phosphide. Growth conditions are listed in Table 1.

In early studies of MOVPE with tertiarybutylphosphine, sulfur was found to be a major contaminant in the organometallic source [1]. As shown in Fig. 2, sulfur doping levels observed in the InP film range from $3.5 \times 10^{15}\,cm^{-3}$ at 520 °C (layers 4 and 5) to below the detection limit of $2.0 \times 10^{14}\,cm^{-3}$ at 610 °C (layers 1 and 7). These results indicate that the sulfur concentration strongly depends on the substrate temperature, but is relatively insensitive to the V/III ratio.

Table 1
Growth conditions for the InP film analyzed by SIMS

Layer no.	V/III ratio	Temperature (°C)	Thickness (μm)
1	32	610	0.25
2 (InGaAsP)	55	610	0.35
3	32	565	0.3
4	32	520	0.3
5	10	520	0.3
6	10	565	0.3
7	20	610	0.6

Shown in Fig. 3 is a SIMS depth profile for silicon in the indium phosphide film. This impurity resulted from residual contamination of the reactor from a prior run that used Si_2H_6 to n-type dope GaAs to $\sim 1.0\times10^{19}\,cm^{-3}$. Before depositing the InP, a different sample platter was inserted through the loadlock, and the system was baked and coated as described in the Experimental Methods section. It can be seen in the figure that the amount of Si decreases from $8\times10^{15}\,cm^{-3}$ to below the detection limit of $4.0\times10^{14}\,cm^{-3}$ as the temperature is reduced from 610 to 520 °C. Comparison of layers 3 and 6 suggests that silicon incorporation depends on the V/III ratio, falling from $1.0\times10^{15}\,cm^{-3}$ to below the detection limit as this variable is lowered from 32 to 10.

The optimal MOVPE process conditions for InP growth with TMIn and TBP may be drawn from the SIMS results. The best compromise appears to be a moderate growth temperature of 565 °C combined with a V/III ratio of 32. Hall measurements have been performed on an InP film, 6.3 μm thick, which was grown at these conditions. The intrinsic carriers were found to be n-type with a concentration of $2.7\times10^{14}\,cm^{-3}$. The carrier mobilities measured for this film at 300 and 77 K are 4960 and 135,000 $cm^2/V\,s$, respectively.

Imori et al. [11] has reported electron mobility data for InP grown with TBP that is slightly better than that reported here. Their value of 167,000 $cm^2/V\,s$ was obtained on material grown at a V/III ratio of 36 in an atmospheric pressure MOVPE reactor, using TBP synthesized in Imori's laboratory. Beccard et al. [12] reported a mobility of 50,000 $cm^2/V\,s$ at 77 K for InP layers grown with TBP at 75 Torr. The results obtained here also may be compared to those reported for MOVPE of InP with phosphine [1,13–16]. These latter studies found that the best material is produced at 600 °C and a V/III ratio between 100 and 500. Under these conditions, the Hall mobilities vary from 100,000 to 264,000 $cm^2/V\,s$ at 77 K, with the highest value reported by Thrush et al. [16]. Thus, we may conclude that InP films generated with TBP exhibit Hall mobilities in about the same range as those prepared with PH_3 [1].

3.2. Aluminum indium phosphide

Presented in Figs. 4 and 5 are the SIMS results recorded for the deposition of $Al_{0.53}In_{0.47}P$ lattice

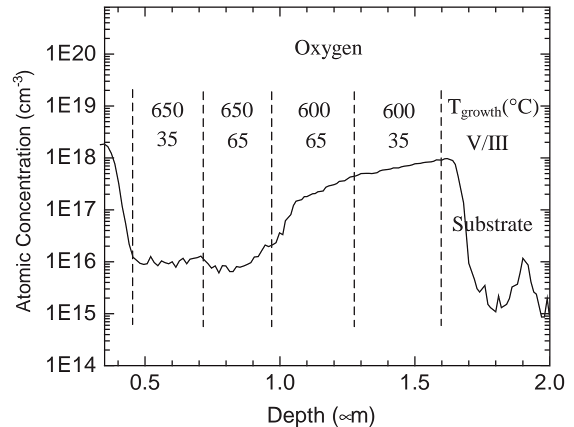

Fig. 4. SIMS profile of oxygen in aluminum indium phosphide.

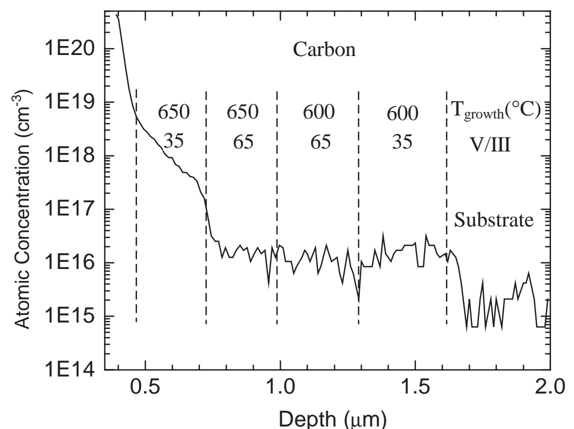

Fig. 5. SIMS profile of carbon in aluminum indium phosphide.

matched to gallium arsenide. The oxygen contamination level decreases dramatically with increasing temperature, but does not change with V/III ratio, within the limited range of values examined. At 600 °C, the O atom concentration is relatively high, ranging between 2.0×10^{17} and $1.0 \times 10^{18}\,cm^{-3}$. By contrast at 650 °C, it falls to $9.0 \pm 1.0 \times 10^{15}\,cm^{-3}$. This latter figure is 10–100 times lower than that reported previously for the deposition of aluminum-containing alloys using either TBP or PH_3 [5–10,17–22]. Among these studies, Kondo et al. [21] observed the lowest oxygen level in AlGaInP, equal to $2.0 \times 10^{16}\,cm^{-3}$. Note that this impurity level was achieved with less aluminum (Al = 0.35) using a V/III ratio of 400 and growth temperature of 690 °C. The results obtained in the present study suggest that by substituting TBP for PH_3, one may substantially reduce the process temperature and chemical usage without sacrificing the material quality.

Inspection of Fig. 5 shows that the carbon doping is insensitive to temperature between 600 and 650 °C, yielding a concentration of 1.1×10^{16} at a V/III ratio of 65. On the other hand, the impurity level appears to be sensitive to the V/III ratio. Reducing the ratio from 65 to 35 at 650 °C causes the carbon concentration to increase to about $5.0 \times 10^{17}\,cm^{-3}$, although the exact value is obscured by contamination from the sample surface. A comparison of Fig. 5 to Fig. 1 indicates that carbon is more of a problem with AlInP than with InP, as one would expect due to the higher Al–C bond strength [23].

Sulfur contamination is below the detection limit of $10^{14}\,cm^{-3}$ in layers deposited at 650 °C. At 600 °C, the sulfur concentration equals $2.0 \times 10^{14}\,cm^{-3}$ at a V/III ratio of 65 and further increases to $4.0 \times 10^{14}\,cm^{-3}$ when the V/III ratio is reduced to 35. The silicon content is seen to be insensitive to either the growth temperature or the V/III ratio in the range examined, and averages $7.0 \times 10^{15}\,cm^{-3}$ in all the layers.

3.3. Gallium arsenide phosphide

The composition of strained $GaAs_yP_{1-y}$ films, ranging in thickness from 20 to 40 nm, was determined by XRD measurements. A distribution coefficient describing the relative incorporation efficiency of the two group V elements is defined as follows [24,25]:

$$\eta = \frac{(N_{As}/N_{P})_{Solid}}{(P_{TBAs}/P_{TBP})_{Gas}}, \quad (1)$$

where N_i is the mole fraction of species i in the GaAsP film, and P_i is the partial pressure of precursor i in the feed to the reactor. Fig. 6 displays the relationship between these two ratios for $GaAs_yP_{1-y}$ MOVPE with TBP and TBAs. The As/P distribution coefficients determined from the slopes of the lines equal 25.4, 15.3 and 8.4 for deposition at 525, 550 and 575 °C, respectively.

Shown in Table 2 are the As/P distribution coefficients obtained in this study and for the growth of GaAsP with PH_3 and AsH_3. The coefficients are found to be 5–10 times smaller for MOVPE with the organometallic compounds, indicating that significantly better control over the alloy composition can be achieved with the alternative sources. The work of Stringfellow et al. [26] suggests that the segregation behavior may be improved further by using AsH_3 in combination with TBP. It should be noted that Leys et al. [27] observed a higher incorporation efficiency for phosphorus in thin compressively strained $GaAs_yP_{1-y}$ on GaP (0 0 1) compared to thick relaxed layers. They attributed this difference to an

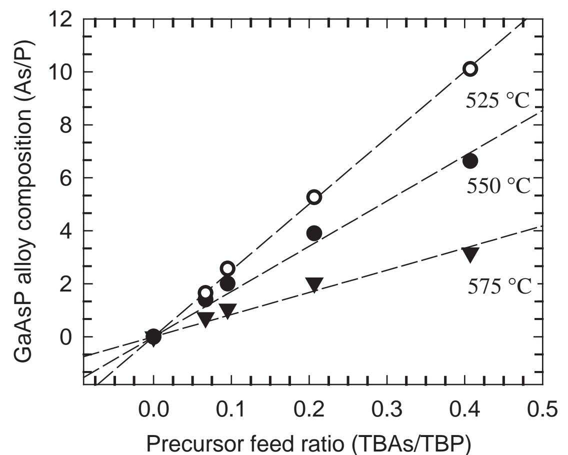

Fig. 6. The As/P distribution coefficient for MOVPE of gallium arsenide phosphide.

Table 2
Arsenic to phosphorus distribution coefficients for GaAsP MOVPE

	Precursors	Growth Temperature (°C)	η	E_A (eV)
This work	TBAs, TBP	525	25.36	1.2
		550	15.30	
		575	8.36	
Fukui et al. [30]	PH_3, AsH_3	600	50	1.2
		750	5	
		800	2	
		850	1.47	
Samuelson et al. [29]	PH_3, AsH_3	650	12.99	1.0
		700	7.14	
		750	3.57	
		800	2.08	
		850	1.33	
Stringfellow [26]	AsH_3, TBP	610	2.29[a]	—

[a]Average value.

effect of the As and P atomic radii on the relative rates of adsorption of the precursors on the semiconductor surface. In the present case for tensile strained $GaAs_yP_{1-y}$ on GaAs (0 0 1), we would not expect this phenomenon to affect the η values.

Samuelson et al. [28,29] have developed a model to explain how the process conditions affect the As/P distribution coefficient:

$$\eta = \frac{(N_{As}/N_P)_{Solid}}{(P_{AsH_3}/P_{PH_3})_{Gas}} = \frac{\alpha}{\beta} \quad (2)$$

with

$$\alpha = k_{As}/d_{As}, \quad \beta = k_P/d_P. \quad (3)$$

Here k_i and d_i are the adsorption and desorption rate constants for As and P. The observed temperature dependency is

$$\frac{\beta}{\alpha} = A \exp(-E_A/kT). \quad (4)$$

An activation barrier of 1.1 ± 0.1 eV (1.0 eV = 23.4 kcal/mole) was observed for GaAsP MOVPE with PH_3 and AsH_3 [29,30]. Shown in Fig. 7 is an Arrhenius plot of the As/P distribution coefficients measured in this study. An activation energy of 1.23 ± 0.05 eV is determined from the slope of the line, consistent with that recorded in the earlier studies.

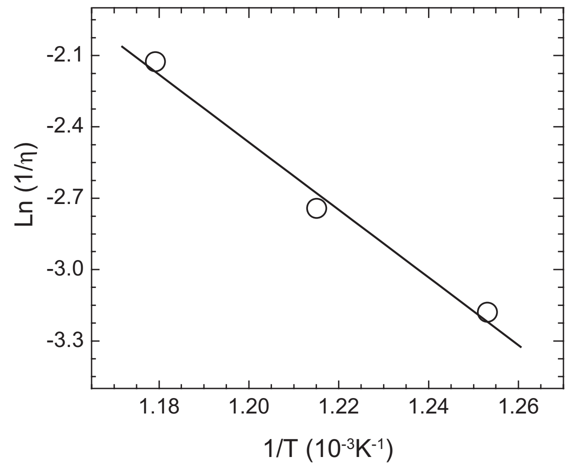

Fig. 7. The dependence of the group V distribution coefficient on temperature for GaAsP MOVPE.

The activation energy, E_A, is most likely associated with the desorption energies for arsenic and phosphorus from the GaAsP surface. This parameter will not change with the choice of group V source, in agreement with the experimental results. The adsorption rate constant may be approximated as $\frac{1}{4}vS_0$, where v and S_0 are the mean molecular speed and reactive sticking probability of the precursor. These terms are relatively temperature insensitive [31,32]. Since the mean molecular speed is about the same for each source, one may assume that the differences in the As/P

segregation coefficients may be attributed to the ratio $S_{0,As}/S_{0,P}$. From Table 2, the η values at 610 °C are estimated to be 4.3, 41.5, and 2.3 for TBAs + TBP, $AsH_3 + PH_3$ and $AsH_3 + TBP$, respectively. These results suggest that at this temperature, TBAs sticks 1.9 times more often than AsH_3, while TBP sticks 18 times more often than PH_3 to the GaAsP surface.

4. Conclusions

We have examined the MOVPE growth of InP, AlInP and GaAsP using tertiarybutylphosphine and tertiarybutylarsine. For GaAsP, the As segregation coefficient varied from 25.4 at 525 °C to 8.4 at 575 °C, indicating that relatively good control can be achieved over the alloy composition in this temperature range. A minimum background carrier concentration of $2.7 \times 10^{14}\,cm^{-3}$ was observed for InP growth at 565 °C and a V/III ratio equal to 32. For AlInP films grown at 650 °C and V/III = 35, the oxygen level was below $10^{16}\,cm^{-3}$. To our knowledge, this is the lowest oxygen level reported to date for MOVPE of this material.

Acknowledgements

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References

[1] G.B. Stringfellow, Organometallic Vapor-Phase Epitaxy: Theory and Practice, second ed., Academic Press, New York, NY, 1999 and references therein.
[2] N.I. Sax, Dangerous Properties of Industrial Materials, Van Nostrand Reinhold, New York, NY, 1979.
[3] G. Miller, Solid State Technol. 32 (1989) 59.
[4] K.L. Hess, R.J. Riccio, J. Crystal Growth 77 (1986) 95.
[5] M. Mannoh, A. Ishibashi, K. Ohnaka, J. Crystal Growth 145 (1994) 158.
[6] W.S. Hobson, M. Geva, in: C.R. Abernathy, C.W. Bates Jr., D.A. Bohling, W. Hobson, Chemical Perspectives of Microelectronic Materials III, Proc. Mater. Res. Soc. 282 (1993) 93.
[7] D.S. Cao, G.B. Stringfellow, J. Electron. Mater. 20 (1991) 97.
[8] M. Mashita, H. Ishikawa, T. Izumiya, Y.S. Hiraoka, Jpn. J. Appl. Phys. 36 (1997) 4230.
[9] S.A. Rushworth, L.M. Smith, M.S. Ravetz, K.M. Coward, R. Odedra, R. Kanjolia, S.W. Bland, F. Dimroth, A.W. Bett, J. Crystal Growth 248 (2003) 86.
[10] W. Stolz, J. Crystal Growth 209 (2000) 272.
[11] T. Imori, T. Ninomiya, K. Ushikubo, K. Kondoh, K. Nakamura, Appl. Phys. Lett. 59 (1991) 2862.
[12] R. Beccard, G. Lengeling, D. Schmitz, Y. Gigase, H. Jürgensen, J. Crystal Growth 170 (1997) 97.
[13] D. Kasemet, K.L. Hess, K. Mohammed, J.L. Merz, J. Electron. Mater. 13 (1984) 655.
[14] M.A. DiForte-Poisson, C. Brylinski, J.P. Duchemin, Appl. Phys. Lett. 46 (1985) 476.
[15] L.D. Zhu, K.T. Chan, J.M. Ballantyne, Appl. Phys. Lett. 47 (1985) 47.
[16] E.J. Thrush, C.G. Cureton, J.M. Trigg, J.P. Stagg, B.R. Butler, Chemtronics 2 (1987) 62.
[17] M.J. Hafich, L.M. Woods, H.S. Kim, G.A. Patrizi, G.Y. Robinson, J. Crystal Growth 127 (1993) 995.
[18] S.A. Rushworth, L.M. Smith, M.S. Ravertz, K.M. Coward, R. Odedra, R. Kanjolia, S.W. Bland, F. Dimroth, A.W. Bett, J. Crystal Growth 248 (2003) 86.
[19] Y. Nishikawa, M. Suzuki, M. Ishikawa, Y. Kokubun, G.i. Hatakoshi, J. Crystal Growth 123 (1992) 181.
[20] J.C. Chen, Z.C. Huang, K.J. Lee, R. Kanjolia, J. Electron. Mater. 26 (1997) 361.
[21] M. Kondo, N. Okada, K. Domen, K. Sugiura, C. Anayama, T. Tanahashi, J. Electron. Mater. 23 (1994) 355.
[22] K.A. Bertness, S.R. Kurtz, S.E. Asher, R.C. Reedy Jr., J. Crystal Growth 196 (1999) 13.
[23] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics 1999–2000: A Ready-reference Book of Chemical and Physical data, eighty-first ed., CRC Press, Boca Raton, FL, 2000.
[24] S. Sugou, A. Kameyama, Y. Miyamoto, K. Furuya, Y. Suematsu, Jpn. J. Appl. Phys. 23 (1984) 1182.
[25] T. Iwamoto, K. Mori, M. Mizuta, H. Kukimoto, Jpn. J. Appl. Phys. 22 (1983) L191.
[26] G.B. Stringfellow, J. Electron. Mater. 17 (1988) 327.
[27] M.R. Leys, H. Titze, L. Samuelson, J. Petruzzello, J. Crystal Growth 93 (1988) 504.
[28] M.L. Hitchman, K.F. Jensen (Eds.), Chemical Vapor Deposition, Principles and Applications, Academic Press, London, 1993.
[29] L. Samuelson, P. Omling, H.G. Grimmeiss, J. Crystal Growth 61 (1983) 425.
[30] T. Fukui, N. Kobayashi, J. Crystal Growth 71 (1985) 9.
[31] Y. Sun, D.C. Law, S.B. Visbeck, R.F. Hicks, Surf. Sci. 513 (2002) 256.
[32] R.I. Masel, Principles of Adsorption and Reaction on Solid Surfaces, Wiley, New York, 1996.