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Growth and Characterization of ZnCdMgSe/ZnCdSe Quantum Wells on InP Substrates for Visible Emitters

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Abstract

High-quality lattice-matched quantum well (QW) structures of ZnCdSe/ZnCdMgSe were grown on InP substrates by molecular beam epitaxy. Emission energies from 2.306 to 2.960 eV were measured by low-temperature photoluminescence for samples with QW thicknesses between 5 and 80 Å. Bandgap measurements indicate that these structures could be used in entirely lattice-matched blue, green, and yellow diode laser structures. Experimental measurements indicated that these structures have very little strain; hence, these materials could possibly be less prone to degradation than the current II-VI blue-green lasers grown on GaAs substrates.

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1. Introduction

Wide bandgap II-VI compounds have applications as blue-green light-emitting diodes (LEDs) and laser diodes. Such laser structures are always grown on GaAs substrates. With appropriate bandgap engineering of II-VI compounds, LED and laser diodes can be developed in the complete range of the visible spectrum. In fact, II-VI compounds were the first materials to be used for the demonstration of blue-green laser diodes [1–5]. Such optoelectronic devices are very useful in high-density optical storage, optical pumping, display systems, covert communications, medical applications, and biological and chemical detection. Currently, fabricated II-VI devices grown on GaAs substrates do not perform well enough to meet the required specifications of useful devices. Specifically, materials get degraded rapidly under current injection, resulting in a very short lifetime. In the last few years, the lifetime of these devices has increased from a few seconds to tens of hours [6].

Blue-green laser diodes currently made are based on II-VI ZnSe materials grown on GaAs substrates. Pseudomorphic structures were obtained by using ZnMgSSe quaternary optical cladding layers and ZnSSe guiding layers. The active region is a thin $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{Se}$ quantum well (QW) containing compressive strain caused by the 1.6 percent lattice mismatch of the epilayer to the substrate GaAs. Ohmic contacts could be successfully obtained on the *p*-type cladding layers by using ZnSe- or ZnTe-graded superlattice [7]. The strain of the ZnCdSe active layer and the formation of misfit dislocations in the contact layer region, because of the relaxation of the very large lattice mismatch between ZnTe and the rest of the structures, are likely sources of degradation of these devices. To alleviate these inherent problems, one must develop other wide bandgap II-VI materials grown on substrates other than GaAs so that they can meet the band structure requirements of laser diodes.

In this report, we present the growth and properties of new ZnCdMgSe/ZnCdSe QW structures that can be used in the design and fabrication of blue-green laser diodes and LEDs. These heterostructures can be grown entirely on InP substrates. The use of InP will allow the growth of a symmetrically strained [8] ZnSe/ZnTe superlattice for ohmic contact formation, eliminating the formation of misfit dislocations in the top contact layer. Finally, the MgSe containing quaternaries may be more easily doped, both *n*- and *p*-type, than the currently used materials [9]. These properties are expected to enhance the performance of LEDs that can be made to emit in the blue, green, and yellow regions.

2. Experiment

We grew the epitaxial layers by molecular beam epitaxy (MBE) in a Riber 2300P growth chamber, which was equipped with conventional effusion cells for Zn, Cd, Mg, Se, As, and ZnCl_2 , and a nitrogen rf plasma source. Before the growth, InP substrates, which were obtained from Sumitomo Electric, were etched in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (4:1:1) for 1 to 2 min. As previously performed by Dai et al [10], we performed oxide desorption of the InP substrate by heating the substrate with an As flux impinging on the InP surface. The best results were obtained by heating the substrate quickly to $\sim 500^\circ\text{C}$, then lowering the temperature to the initial growth temperature of 170°C . Once the growth was initiated, after 1 min, we raised the growth temperature to the optimum of 270°C . During the removal of the oxide, As flux was kept on the substrate to suppress the P evaporation from the InP surface [10,11]. Epilayers and QW structures given in this report were typically grown at 270°C under group VI rich conditions. The II-VI flux ratio, as measured with an ionization gauge in the growth position, was kept at 4. To obtain two-dimensional nucleation on the InP substrate, we started the growth at 170°C . Under these conditions, we routinely obtained featureless, defect-free surfaces and two-dimensional nucleation of the II-VI layer on the InP substrate, as indicated by the presence of a streaky pattern of reflected high-energy electron diffraction (RHEED) throughout the nucleation and growth. After 1 min at 170°C , growth was interrupted, leaving the Se flux on the epilayer. The growth temperature was increased to 270°C . Once we stabilized the temperature, the growth was resumed by opening the shutters for group II sources. Adding this new step, we have observed further improvements in epitaxial layer quality.

The ZnCdMgSe and ZnCdSe layers and QW structures were characterized by photoluminescence (PL) at 10 and 300 K, using 325 nm of output of a He-Cd laser. We determined lattice mismatch and crystalline quality of the ZnCdMgSe and ZnCdSe layers by single-crystal and double-crystal x-ray measurements. Layers of lattice-matched ZnCdSe 1 μm thick and grown on InP using the growth conditions described in the previous paragraph show excellent PL properties, with 8-meV full width at half maximum (FWHM) and near absence of defect-related deep-level emission. Double-crystal x-ray measurements exhibited epilayer peaks with 270 arcsec FWHM, indicating good crystal quality. We grew lattice-matched ZnCdMgSe quaternary layers with a bandgap ranging from 2.3 to 3.2 eV [12,13].

QW structures nearly lattice-matched were grown using ternaries of nominal composition $\text{Zn}_{0.55}\text{Cd}_{0.45}\text{Se}$ and ZnCdMgSe quaternaries with 54% Mg. The structure consisted of a 1- μm -thick ZnCdMgSe barrier layer, a ZnCdSe QW, a top 1000- \AA -thick ZnCdMgSe barrier layer, and a 50- \AA ZnSe cap layer. We also grew some structures containing two QWs, separated by a 500- \AA barrier. Quantum wells from 5 to 80 \AA were investigated. In these structures, the ZnCdMgSe barrier layers are well lattice-matched to InP, and the ZnSe QW is slightly strained with about

-0.5 percent lattice-mismatch. This mismatch is because two different Cd fluxes are needed for the growth of exactly lattice-matched ZnCdMgSe and ZnCdSe to InP. This problem could be solved by having two Cd cells in the growth chamber. Alternatively, growth could be interrupted for adjustments of the Cd flux between growth of the quaternary and ternary layers. This latter option may contaminate the interface.

3. Results and Discussion

The PL spectrum taken at a low temperature indicated variations in emission energy levels for varying thickness of the QWs. The low-temperature PL spectrum of a QW structure is shown in figure 1. In the figure, the marked arrow indicates the signal of a 1- μm ZnCdSe layer with the same composition as the QW, and the layer exhibits a bandgap of 2.278 eV. The bandgap for the ZnCdMgSe barrier layer was detected at 2.980 eV. The emission from the nominally 28- \AA -thick QW was detected at 2.45 eV, indicating a quantum shift of 173 meV. An emission linewidth of 26 meV as shown in figure 1 indicates that the interfaces at the QW are smooth and abrupt. Figure 2 shows the room-temperature PL, which also indicates a very strong emission, confirming the high quality of the sample.

We used QWs of different thicknesses for the measurements of emission energy and plotted them as shown in figure 3. The quaternary barrier layers had a bandgap ranging between 3.0 and 3.1 eV, as shown by a bar on the left axis of the plot. For a thick ZnCdSe sample with the composition used in the QW, the bandgap is about 2.28 eV, which is marked by another bar at the right axis of the plot. A dashed line connecting the data is drawn to highlight the range over which the emission energy varies for these samples. Similar data from strained-layer ZnCdSe/ZnSse QWs grown on GaAs substrates [13] are also shown in figure 3. These QW structures are like those currently used in blue-green lasers reported by Jeon et al and Gaines et al [2,4]. The comparison shows that the samples in discussion have a much larger tunability range of the quantum emission wavelength. As seen by the dashed lines in figure 3, the tunability of

Figure 1. Low-temperature PL spectrum of ZnCdMgSe/ZnCdSe quantum well at 10 K.

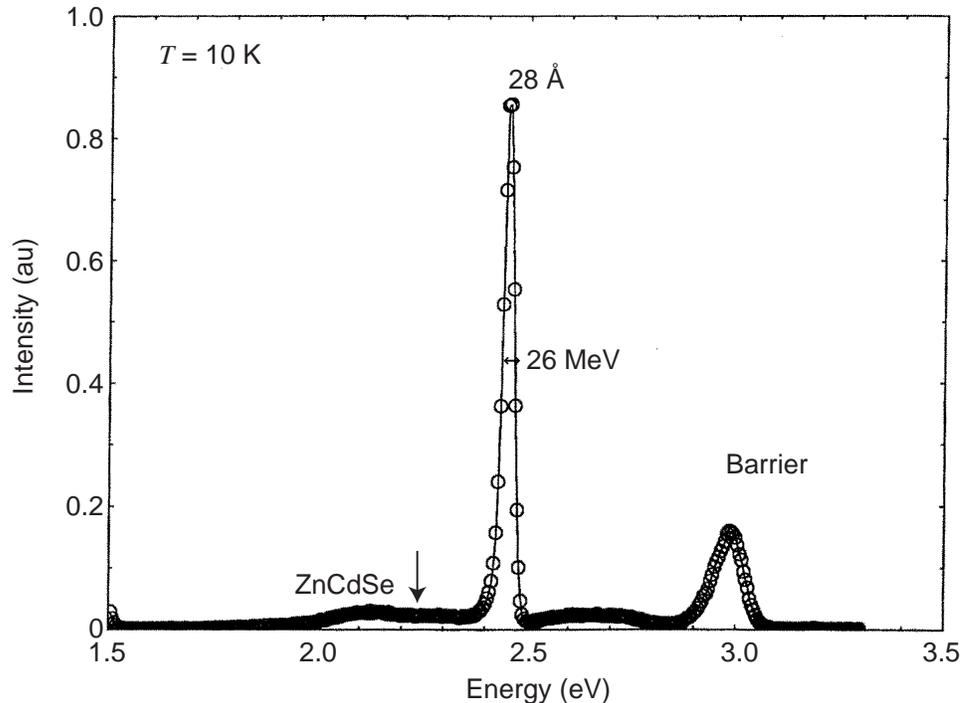


Figure 2. Room-temperature PL spectrum of ZnCdMgSe/ZnCdSe quantum well.

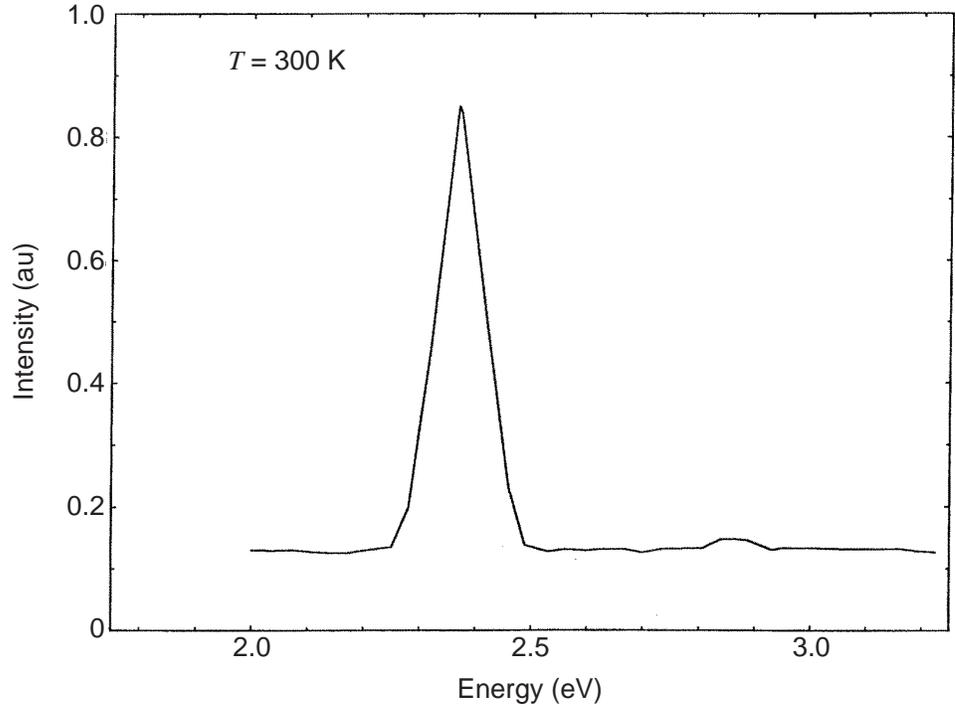
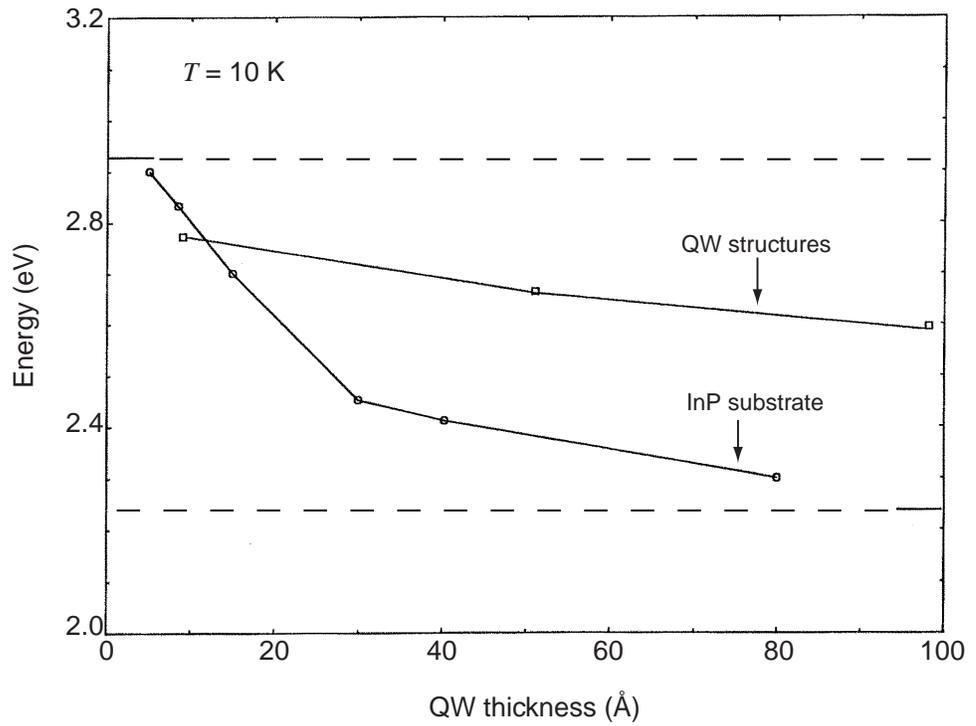


Figure 3. Emission energy range (shown by dashed lines) of ZnCdMgSe/ZnCdSe QW structures grown on InP substrates and ZnSse/ZnCdSe QW structures grown on GaAs substrates.



emission energy range is about 800 meV for the ZnCdMgSe/ $\text{Zn}_{0.55}\text{Cd}_{0.45}\text{Se}$ structures grown on InP, whereas the QN structures grown on GaAs substrates have a possible emission energy range of 230 meV. Therefore, it is possible to obtain different emission wavelengths covering nearly all the visible spectrum range by varying the QW thickness of the particular samples under discussion. This visible spectrum range increases if QW structures are perfectly lattice-matched to ZnCdSe with a bandgap of 2.2 eV and to ZnCdMgSe with a bandgap of 3.2 eV or higher and if ZnCdSe and ZnCdMgSe are used in the structure. Furthermore, even the blue-emitting QW (2.76 eV) has a confinement energy of about 250 meV.

The confinement energy of ZnCdSe/ZnCdMgSe QW grown on GaAs substrates, emitting at the same energy, is only about 100 meV. High confinement energy is a very desirable feature for good device performance, such as low temperature dependence of the laser threshold [15]. From the width of the PL emission lines, one can assess the quality of quantum structures. Figure 4 shows the plot of the FWHM of the PL emission lines measured at 10 K as a function of QW thicknesses. As can be seen in the figure, the linewidth fluctuates especially for a QW less than 40 Å thick, indicating roughness at the QW interfaces. These results are very consistent with the observations of the RHEED pattern made during the growth of these samples. In particular, we observed streaky RHEED patterns for samples that exhibited narrow linewidths. In spite of the variations, data in figure 4 indicate that some structures that were grown had narrow linewidths, thus indicating smooth interfaces in the grown samples.

These QW structures, being entirely lattice-matched, are likely to be less susceptible to degradation than the strained QW materials presently used and should be attractive for improved blue LEDs. Figure 5 shows a possible lattice-matched laser structure with an active area made up of a QW like the one described in this report. The light-emitting region in a ZnCdSe QW is centered in a ZnCdMgSe quaternary light-guiding layer and lattice-matched to the InP substrate. For the cladding layer, a second quaternary composition, also lattice-matched to the substrate, with a larger bandgap is used. Chlorine from a zinc chloride source and nitrogen from an rf plasma source are expected to provide *n*- and *p*-type doping, respectively, as they do in other ZnSe-based alloys. Emission between 2.2 and 2.8 eV (0.54–0.43 μm) is possible from this structure if the thickness of the QW is modified. A symmetrically strained ZnSe and ZnTe superlattice without strain and dislocation in the structure can be used as the top contact layer. We are also suggesting an InGaAs lattice-matched buffer layer, which is expected to improve the II-VI/III-V interface quality as shown in the figure 5.

Figure 4. FWHM of QW emission lines as a function of QW thickness.

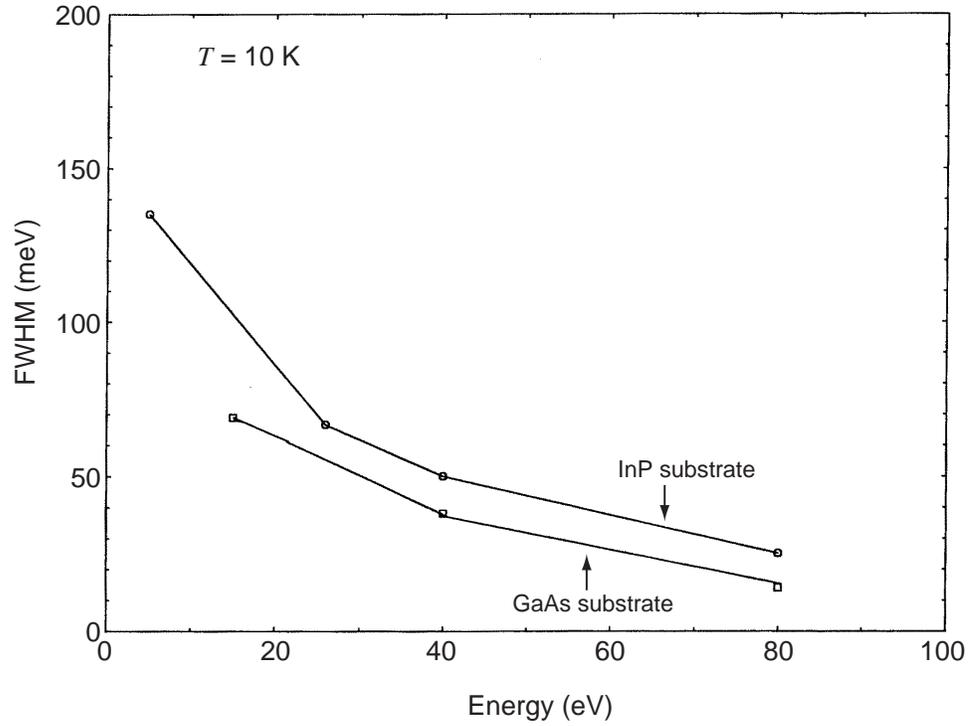
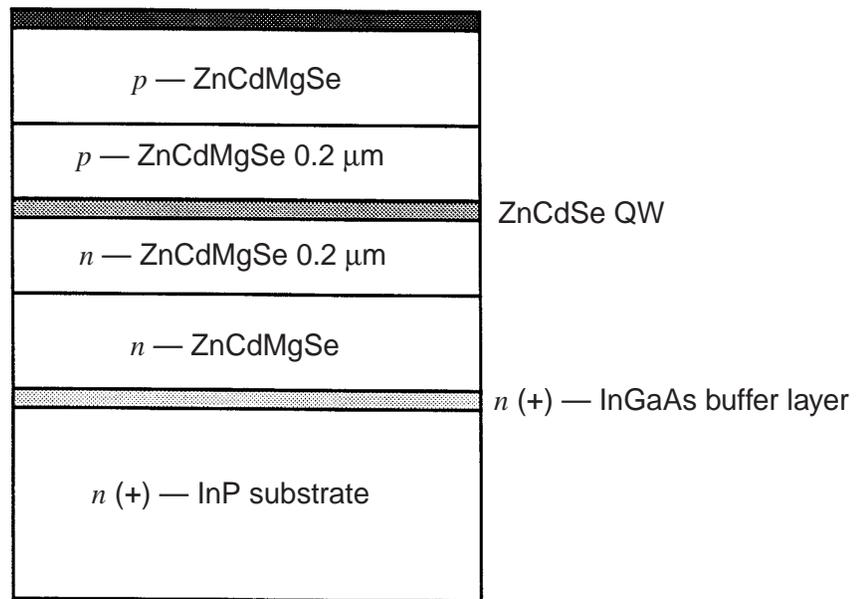


Figure 5. Proposed entirely lattice-matched II-VI laser structure on InP with possible emission energy range of 2.2 to 2.8 eV.

$p (+)$ — (ZnSe/ZnTe) strained-layer superlattice



4. Conclusions

In conclusion, nearly lattice-matched QW structures of ZnCdMgSe and ZnCdSe were grown on InP substrates. Low-temperature PL emission from 2.306 to 2.960 eV was obtained when the QW thickness was varied between 5 and 80 Å. High PL efficiency at 10 K and room-temperature was observed from these samples. Sharp PL lines, consistent with high-quality interfaces, were obtained in many samples.

For entirely lattice-matched laser structures, one can use these QW structures as the active region. We have also proposed a laser structure that is an entirely lattice-matched structure and hence is expected to be less prone to degradation than the current blue-green diodes reported in the literature.

References

1. M. A. Hasse, J. Qiu, J. M. DePuydt, and H. Cheng, *Appl. Phys. Lett.* **59** (1991), 1272.
2. H. Jeon, J. Ding, A. V. Nurmikko, W. Xie, D. C. Grillo, M. Kobayashi, R. L. Gunshor, G. C. Hua, and N. Otsuka, *Appl. Phys. Lett.* **60** (1992), 2025.
3. Z. Yu, J. Ren, B. Sneed, K. A. Bowers, K. J. Gosset, C. Boney, Y. Lansari, J. W. Cook, Jr., J. F. Schetzina, G. C. Hua, and N. Otsuka, *Appl. Phys. Lett.* **61** (1992), 1266.
4. J. M. Gaines, R. R. Drenten, K. W. Haberen, T. Marshall, P. Menz, and J. Petruzzello, *Appl. Phys. Lett.* **62** (1991), 2462.
5. N. Nakayama, S. Itoh, T. Ohata, K. Nakano, H. Okuyama, M. Ozawa, A. Ishibashi, M. Ikeda, and Y. Mori, *Electron. Lett.* **29** (1993), 1488.
6. N. Nakano, S. Tomiya, M. Ukita, H. Yoshida, S. Itoh, E. Morita, M. Ikeda, and A. Ishibashi, presented at 1995 Electronics Material Conference, Charlottesville, VA (1995).
7. Y. Fan, J. Han, L. He, J. Saraie, R. L. Gunshor, M. Hagerott, H. Jeon, A. V. Nurmikko, G. C. Hua, and N. Otsuka, *Appl. Phys. Lett.* **61** (1992), 3160.
8. M. C. Tamargo, R. Hull, L. H. Greene, J. R. Hayes, and A. Y. Cho, *Appl. Phys. Lett.* **46** (1985), 569.
9. D. J. Chadi, *Phys. Rev. Lett.* **72** (1994), 534.
10. N. Dai, A. Cavus, R. Dzakpasu, M. C. Tamargo, F. Semendy, N. Bambha, D. M. Hwang, and C. Y. Chieu, *Appl. Phys. Lett.* **66** (1995), 2742.
11. M. C. Tamargo, N. Dai, A. Cavus, R. Dzakpasu, W. Krystek, F. Pollak, F. Semendy, N. Bambha, P. Boyd, D. M. Hwang, and C. Y. Chen, *Proc. SPIE*, **70** (1994), 2346.
12. M. C. Tamargo, A. Cavus, N. Dai, N. Bambha, A. Gray, F. Semendy, W. Krystek, and F. Pollak, *Proceedings of the International Conference on Semiconductor Heteroepitaxy*, Montpellier, France (1995).
13. Y. Wu, K. Ichino, Y. Kawakami, S. Fujita, and Sg. Fujita, *Jpn. J. Appl. Phys.* **31** (1992), 3608.
14. M. Buijs, K. Shahzad, S. Flamholtz, K. Haberen, and J. Gaines, *Appl. Phys. Lett.* **67** (1995).

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