行政院國家科學委員會專題研究計畫　期中進度報告

自組成氮化銦鎵量子點研究(2/3)

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奈米國家型計畫執行報告

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主持人：台灣大學光電所　楊 志 忠

一、計畫之執行及所遭遇困難

本年度執行中遭遇到主要的困難為在建立一新無塵室來安置新購買之 MOCVD 機台之過程中，因政府採購法之僵硬規定，開標過程中先後流標三次，再加上因競標結果，成交金額低，造成廠商之進度拖延，因而整個 MOCVD 開始運轉時間延後半年，稍微影響研究進度。所幸目前困難皆已排除，生長本研究計畫所需氮化銦鎵奈米結構已順利展開，樣品品質相當不錯。

本年度中執行主要工作包括：

1. 高銦濃度之 InGaN/GaN 量子井結構生長，如過去研究所預測，所生長出來的量子井其實是銦成份較高之奈米顆粒，這些顆粒乃是發光之來源。
2. 以飛秒激發—探測方法探討上述奈米結構之超快載子／激子動態，包括同色及不同色之實驗。
3. 以高解析度穿透式電子顯微鏡分析相關奈米結構。
4. 開始以此種奈米結構製作高效率發光二極體，朝向白光發展。

二、重要研究成果貢獻

本計畫第二年度重要研究成果可歸納為以下幾點：

1. Cluster Size and Composition Variations in an InGaN Thin Film of Yellow Emission upon Thermal Annealing

We study the thermal annealing effects on the size and composition variations of indium-aggregated clusters in two InGaN thin films with photoluminescence (PL) in the yellow and red ranges. The research methods include optical measurement, nano-scale material analysis, and theoretical calculation. Such a study is important for determining the relation between the band gap and the average indium content of InGaN. In one of the samples, the major part of the PL spectrum is shifted from the yellow band into the blue range upon thermal annealing. In the other sample, after thermal annealing, a broad spectrum covering the whole visible range is observed. Cathodo-luminescence (CL) spectra show that the spectral changes occur essentially in the photons emitted from the shallow layers of the InGaN films. Photon emission spectra from the deeper layers are essentially unaffected by thermal annealing. The spectral changes upon thermal annealing are mainly attributed to the general trend of cluster size reduction. This interpretation is supported by the CL, x-ray diffraction and high-resolution transmission electron microscopy (HRTEM) results. To obtain a basic physics picture behind the spectral blue shift upon thermal annealing in the yellow emission sample, we theoretically study the quantum-confinement effects of InGaN clusters based on a quantum box model. The theoretical results can generally explain the large blue shift of PL spectral peak position.

2. Nanostructures and Carrier Localization Behaviors of Green-luminescence InGaN/GaN Quantum-well Structures of Various Silicon-doping Conditions

The results of photoluminescence (PL), detection-energy-dependent photoluminescence excitation (DEDPLE), excitation-energy-dependent photoluminescence (EEDPL), and strain state analysis (SSA) of three InGaN/GaN quantum-well (QW) samples with silicon doping in the well, barrier and an undoped structure are compared. The SSA images show strongly clustering nanostructures in the barrier-doped sample and relatively weaker composition fluctuations in the undoped and well-doped samples. Differences in silicon doping between the samples give rise to the differences in DEDPLE and EEDPL spectra, as a result of the differences in carrier localization. Also, the PL results provide us clues for speculating that the S-shape PL peak position behavior is dominated by the quantum-confined Stark effect in an undoped InGaN/GaN QW structure.

3. Improvements of InGaN/GaN Quantum Well Interfaces and Radiative Efficiency with InN Interfacial Layers

The optical properties and nanostructures of two InGaN/GaN quantum-well (QW) samples of slightly different structures are compared. In one of the samples, InN interfacial layers of a few monolayers are added to the structure between wells and barriers for improving the QW interface quality. Compared with the standard barrier-doped QW sample, the addition of the InN interfacial layers does improve the QW interface quality and hence the photon emission efficiency. The strain state analysis images show the high contrast between the clear QW interface in the sample with InN layers and the diffusive QW boundaries in the reference sample. The detection-energy-dependent photoluminescence excitation data reveal the consistent results.

4. Carrier Relaxation in InGaN/GaN Quantum Wells with nm-scale Cluster Structures

We perform fs degenerate pump-probe experiments on an InGaN thin film, in which piezoelectric fields exist. The observed temperature-, pump-energy-, and pump-intensity-dependent variations of ultrafast carrier dynamics manifest the Franz-Keldysh oscillation (FKO) phenomenon. The carrier dynamics is controlled by the shift of effective band gap and hence the behavior of band filling, which are determined by the combined effect of carrier screening, band-gap renormalization, and phonon effect. Two-photon absorption and free-carrier absorption can be observed when the band filling effect is weak. The calibrated FKO period of 120 meV is consistent between the measurements of absorption and pump-probe experiment. From this value, the piezoelectric field in the InGaN film is calibrated to be around 0.22 MV/cm.

5. Excitation power dynamics of photoluminescence in InGaN/GaN quantum wells with enhanced carrier localization

Excitation-power dynamics of near-band-edge photoluminescence (PL) peak position in $In_xGa_{1-x}N$/GaN multiple quantum wells (x~0.15) was analyzed as a function of well width. The analysis was based on energy reference provided by photoreflectance (PR) spectra. The difference in spectral position of the PR feature and low-excitation PL band (the Stokes Shift) revealed carrier localization energy, which exhibited a remarkable sensitivity to the well width, increasing from 75 meV in 2 nm wells to about 250 meV in 4 nm wells. Meanwhile collating of the PR data with the flat-band model for the optical transition energy in quantum wells rendered a relatively weak (0.5 MV/cm) built-in piezoelectric field. The blueshift of the PL peak position with increasing photoexcitation power density was shown to be in qualitative agreement with the model of filling of the band-tail states with some contribution from screening of built-in field in the thickest (4 nm) wells. Increased incident photon energy resulted in an additional blueshift of the PL peak, which was explained by a nonthermalized distribution of localized carriers and/or carrier localization in the interface region. Our results are consistent with a concept of emission from partially relaxed large In-rich regions with internal band potential fluctuations, which are enhanced with increasing the growth time.

6. Ultrafast Carrier Dynamics in an InGaN Thin Film

We perform fs degenerate pump-probe experiments on an InGaN thin film of 800 nm in thickness. The observed temperature-, pump-photon-energy-, and pump-intensity-dependent variations of ultrafast carrier dynamics manifest the variation of the space-averaged density of state with energy level in this sample. The carrier dynamics is controlled by the shift of effective bandgap and hence the behavior of band filling, which are determined by the combined effect of bandgap renormalization and phonon effect (bandgap shrinkage with increasing temperature). Two-photon absorption and free-carrier absorption can be observed when the corresponding density of state is low and hence the band-filling effect is weak. The variation of the space-averaged density of state with energy level can be due to the existence of indium-composition-fluctuation nanostructures, which is caused by the spinodal decomposition process, in the sample.

7. Exciton hopping in InGaN multiple quantum wells

The dynamics of photoexcited excitons in thin InGaN/GaN multiple quantum wells (QW's) with different In contents was studied by comparing the experimental data obtained by photoluminescence (PL), PL excitation, and photoreflectance spectroscopy techniques with the results of Monte Carlo simulations of exciton hopping. The temperature dependence of the PL linewidth was demonstrated to be in a fair agreement with the model of phonon-assisted exciton in-plane hopping within In-rich regions with inhomogeneous broadening taken into account. The band potential fluctuations, which scale the dispersion of localized states the excitons are hopping over, were attributed to compositional disorder inside the In-rich regions. Meanwhile, the inhomogeneous broadening was explained by variation in mean exciton energy among the individual In-rich regions. For typical 2.5-nm-thick $In_xGa_{1-x}N$ (x<0.22) QW's, the simulation revealed fluctuations of the band potential (31 meV) with additional inhomogeneous broadening (29 meV) and a crossover from a nonthermalized to thermalized exciton energy distribution at about 150 K. Both the fluctuations and inhomogeneous broadening showed an enhancement with increasing of In content. Simultaneously, a Bose-Einstein-like temperature dependence of the exciton energy in the wells was extracted using data on the PL peak position. The dependence exhibited a fair conformity with the photoreflectance data. Moreover, the density of localized states used in the simulation was found to be consistent with the PL excitation spectrum.

8. Effects of Silicon Doping on the Nanostructures of InGaN/GaN Quantum Wells

We compare the results of strain state analysis (SSA) and photoluminescence (PL) of six InGaN/GaN quantum well samples with un-doped, well-doped, and barrier-doped structures. Based on the SSA images, a strain relaxation model is proposed for describing the nanostructure differences between the three sets of sample of different doping conditions. In the barrier-doped samples, the hetero-structure-induced strains are fully relaxed such that spinodal decomposition is effectively induced. Therefore, strongly clustering nanostructures are observed. In the well-doped samples, strains are partially relaxed and the spinodal decomposition process can be slightly induced. Hence, weaker composition fluctuations are observed. Then, in the un-doped samples, the un-relaxed strains result in higher miscibility between InN and GaN, leading to the relatively more uniform composition distributions. Between the low- and high-indium samples, higher indium content leads to a stronger clustering behavior. The strain relaxations in the well-doped and barrier-doped samples result in their unclear S-shape behaviors of PL spectral peaks. The enhanced carrier localization and reduced quantum-confined Stark effect in the barrier-doped samples are responsible for their significant increases of radiative efficiency.

9. Effects of Interfacial Layers in InGaN/GaN Quantum Well Structures on Their Optical and Nanostructure Properties

We compare the optical properties and material nano-structures between four InGaN/GaN multiple quantum-well (QW) samples of different interfacial layers. In two of the four samples, InN interfacial layers are inserted between the wells and barriers for improving the QW quality and hence the light emission efficiency. Comparing with a widely used barrier-doped QW structure, the insertions of the InN interfacial layers (silicon-doped or un-doped) do enhance the photon emission efficiencies. Between the two samples of InN interfacial layers, the one with intrinsic InN interfacial layers has the higher photoluminescence (PL) and electro-luminescence (EL) efficiencies. Cluster structures are clearly observed in this sample, resulting in strong carrier localization. In this sample, we also observe a temperature-dependent S-shape variation in PL spectral peak, a strong photoluminescence excitation (PLE) intensity, and a steep PL decay time variation beyond its peak in temperature dependence. On the other hand, both carrier localization and quantum-confined Stark effect (QCSE) are relatively weaker in another sample, which includes silicon-doped InN interfacial layers. Then, the broadening of the InGaN well layers in the other sample by inserting silicon-doped InGaN interfacial layers leads to the sharpest cluster structures and the strongest carrier localization among the four samples. Therefore, in this sample we observe quite high PL and EL efficiencies, increasing EL spectral peak energy with temperature, a strong PLE intensity, and a steep PL decay time variation beyond its peak in temperature dependence. Comparing with the aforementioned samples, the widely used QW structure (the reference sample) shows the lowest PL and EL emission efficiencies, the smallest PL and EL emission photon energies, and the generally longest PL decay times. The QCSE is the strongest in this sample.

10. Non-degenerate fs Pump-probe Study on Clustered InGaN with Multi-wavelength Second-harmonic Generations

Non-degenerate fs pump-probe experiments in the UV-visible range for ultrafast carrier dynamics study of InGaN with adjustable pump and probe photon energies are implemented with simultaneously multi-wavelength second-harmonic generation (SHG) of a 10 fs Ti:sapphire laser. The multi-wavelength SHG is realized with two β-barium borate crystals of different cutting angles. The full-widths at half-maximum of the SHG pulses are around 160 fs, which are obtained from the cross-correlation measurement with a reverse-biased 280-nm light-emitting diode as the two-photon absorption photo-detector. Such pulses are used to perform non-degenerate pump-probe experiments on an InGaN thin film, in which indium-rich nano-clusters and compositional fluctuations have been identified. Relaxation of carriers from the pump level to the probe one through the scattering-induced local thermalization (<1 ps) and then the carrier-transport-dominating global thermalization (in several ps) processes is observed.

11. Ultrafast Biexciton Dynamics in a ZnO Thin Film

The emission lines of biexciton and donor-bound biexciton are observed in a high-quality ZnO thin film sample with time-resolved photoluminescence (TRPL) measurement. The TRPL intensity profiles reveal the formation sequence of various types of exciton. After free excitons are first generated, part of them is trapped by neutral donors to form donor-bound excitons. The other part contributes to the generation of biexcitons through free exciton scattering. Next, a donor-bound biexciton is generated through the trapping of a biexciton or two free excitons by a neutral donor or the trapping of a free exciton by a donor-bound exciton. Except donor-bound exciton, the relaxations of all other exciton states show two decay stages. Either the increasing or decreasing trends of the calibrated decay times in increasing the excitation power are well interpreted with a four-level model.

The related SCI journal publications include (in the last two years):

1. Fang-Yi Jen, Yen-Cheng Lu, Cheng-Yen Chen, Hsiang-Chen Wang, C. C. Yang, Bao-ping Zhang, and Yusaburo Segawa, “Ultrafast Biexciton Dynamics in a ZnO Thin Film,” submitted to Applied Physics Letters.
2. Hsiang-Chen Wang, Yen-Cheng Lu, Cheng-Yen Chen, and C. C. Yang, “Non-degenerate fs Pump-probe Study on Clustered InGaN with Multi-wavelength Second-harmonic Generations,” submitted to Optics Express. (SCI)
3. Yung-Chen Cheng, Cheng-Ming Wu, C. C. Yang, Gang Alan Li, Andreas Rosenauer, Kung-Jen Ma, Shih-Chen Shi, and L. C. Chen, “Effects of Interfacial Layers in InGaN/GaN Quantum Well Structures on Their Optical and Nanostructure Properties,” accepted fro publication in J. Applied Physics. (SCI)
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5. S. Miasojedovas, S. Jursenas G. Kurilcik, A. Zukauskas, M. Springis, I. Tale, and C. C. Yang, “Stimulated Emission in InGaN/GaN Multiple Quantum Wells with Different Indium Contents,” *ACTA PHYSICA POLONICA A*, Vol. 107, pp. 256-260, 2005.
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11. Hsiang-Chen Wang, Yen-Cheng Lu, Chih-Chung Teng, Yung-Sheng Chen, C. C. Yang, Kung-Jen Ma, Chang-Chi Pan and Jen-Inn Chyi, "Ultrafast Carrier Dynamics in an InGaN Thin Film," J. Applied Physics, Vol. 97, No. 3, pp. 033704-1-4, 2005. (SCI) Also, it was selected for the 2005 issue of Virtual Journal of Ultrafast Science (American Physical Society and the American Institute of Physics).
12. K. Kazlauskas, G. Tamulaitis, J. Mickevičius, E. Kuokštis, A. Žukauskas, Yung-Chen Cheng, Hsiang-Cheng Wang, Chi-Feng Huang, and C. C. Yang, "Excitation power dynamics of photoluminescence in InGaN/GaN quantum wells with enhanced carrier localization," J. Applied Physics, Vol. 97, pp.013525-013531, 2004. (SCI)
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21. Shih-Wei Feng, En-Chiang Lin, Tsung-Yi Tang, Yung-Chen Cheng, Hsiang-Chen Wang, C. C. Yang, Kung-Jen Ma, Cheng-Hsing Shen, L. C. Chen, K. H. Kim, J. Y. Lin and H. X. Jiang, “Thermal Annealing Effects of an InGaN Film with an Avearge Indium Mole Fraction of 0.31,” Applied Physics Letters, Vol. 83, No. 19, pp. 3906-3908, November 2003. (SCI)
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三、九十四年度計畫執行內容修正

由於有了長晶之 MOCVD 設備，我們可以更積極發展奈米研究，為此，我們修正研究方向如下：

1. 生長高銦濃度之氮化銦鎵奈米結構，以產生高效率之黃光及紅光。

2. 組裝奈米螢光量測裝置，以探討單顆奈米結構之載子／激子動態。

3. 以此奈米結構，配合其他如 CdSe 量子點或螢光粉製作高效率之白光光源。

4. 繼續奈米結構之材料分析。