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Blue-Shifted Photoluminescence from GaAs/AlGaAs Quantum-Well Box Fabricated by Low-Damage Wet Chemical Etching

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Ultrafine (~35nm) GaAs/AlGaAs quantum-well box (QWB) structures were fabricated successfully by using electron beam lithography and wet chemical etching. Owing to the low-damage etching technique employed, we have observed bright photoluminescence (PL) of the QWB that showed clear blue-shift from that of as-grown single quantum-well. PL intensity of the QWB was further enhanced by an $(NH_4)_2S_x$ treatment indicating that the surface-damage introduced through the etching process was effectively reduced by the treatment.

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1. Introduction

Multi-dimensional quantum confinement structures such as quantum-well wire (QWW) and quantum-well box (QWB) are currently gaining much interest because of their feasibility of realizing various high-performance optical/electrical devices such as very low threshold semiconductor lasers.[1] For this reason, a variety of nanofabrication techniques have been investigated.[2-12] Selective growth[2-3] and growth on patterned substrate[4-5] are damageless processes, so that QWWs and QWBs fabricated by these techniques show intense photoluminescence (PL). However, these techniques are subject to regulations on shape and materials arising from growth mechanisms involved, which leads to difficulties in theoretical analysis of the quantized state and limits their applicability to device fabrication. Electron beam (EB) lithography in combination with dry etching techniques[6-8] such as reactive ion etching (RIE) and reactive ion beam etching (RIBE) is also often used in nanofabrication, where EB-drawn fine patterns can be accurately transferred from the resist to the semiconductor substrate by the dry process. The plasma-induced damage inherent in dry process, however, causes severe degradation of optical/electrical properties especially in GaAs/AlGaAs system; in fact, PL could not be observed in GaAs/AlGaAs QWW array fabricated by RIE unless the array was buried by metalorganic vapor phase epitaxial regrowth.[6]

In the present study, we have developed a new low-damage fabrication technique of semiconductor nanostructures combining EB lithography with wet chemical etching,[9-12] which relies on pure chemical reaction and introduces less damage than dry etching. By appropiately choosing the mask pattern orientation with respect to the crystal axis and making use of undercutting, ultrafine (~35nm) GaAs/AlGaAs QWBs with smooth side walls, which would never be obtained by dry etching, were fabricated. PL spectrum of the GaAs/AlGaAs QWBs has been measured and found to exhibit a clear blue shift arising from three dimensional quantum confinement. It has also be found that PL intensity of the QWBs was further enhanced by an $(NH_4)_2S_x$ treatment indicating that the surface-damage introduced through the etching process was effectively alleviated by the treatment.

2. Fabrication Process

Anisotropy is certainly an important feature of wet etching that should be taken into consideration when it is applied to nanofabricatons. It is well known that ordinary mesa and reversed-mesa are obtained when the stripe mask patterns running parallel to $<1\bar{1}0>$ and $<110>$ directions, respectively, are transferred by an wet etching on a (001) GaAs substrate. On the other hand, sidewalls perpendicular to the substrate surface is obtained when the stripe axis is tilted by 45° with respect to $<110>$ direction.[13] This property, which has been successfully applied in fabrcation of wire structures[12], can be utilized in fabrication of whisker structures as shown in Fig. 1; by preparing an etching window composed of two dimensienal array of stripes on a GaAs substrate with their axes parallel to the <100> and <010> directions and introducing a deep undercut in wet etching through an etchant of H_2SO_4-H_2O_2-H_2O in reaction rate-limited region, GaAs whiskers with a high aspect ratio were fabricated.

We have applied this technique to fabrication of

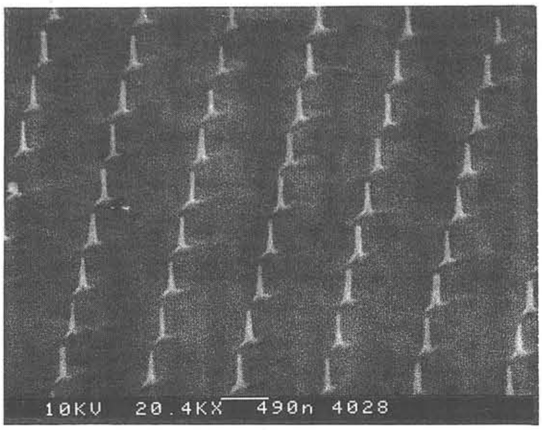

Fig. 1 Secondary electron image (SEI) of GaAs whisker-like structure with the dimension of 40-60nm width and 550nm height.

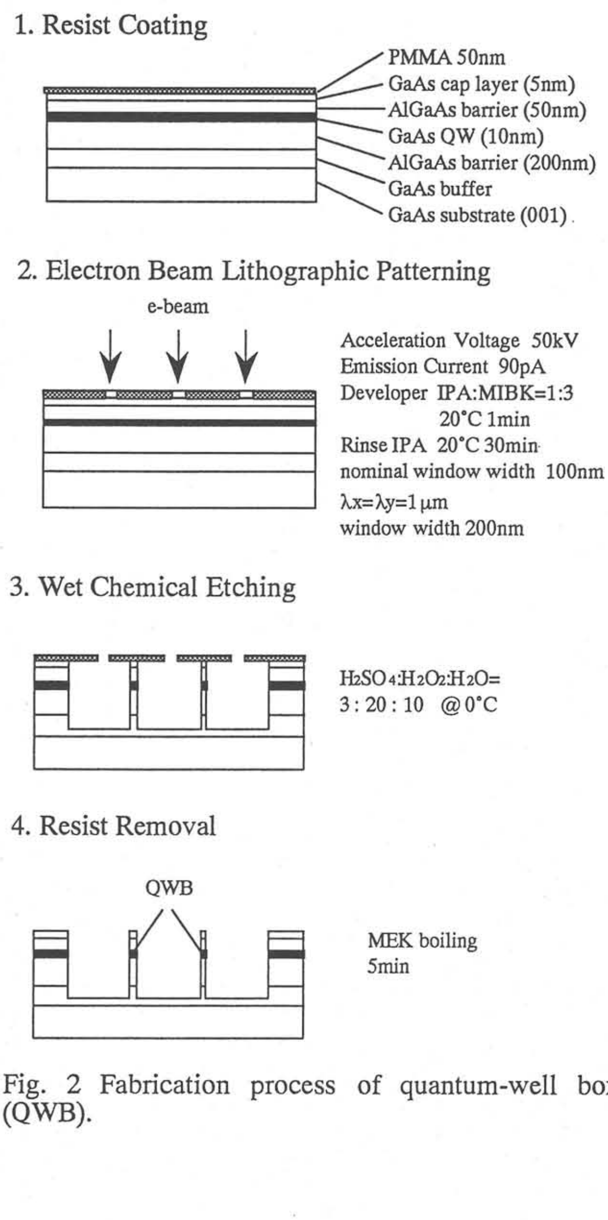

Fig. 2 Fabrication process of quantum-well box (QWB).

GaAs/AlGaAs QWB array. Figure 2 shows the flow of the QWB fabrication process. A GaAs/AlGaAs single quantum-well (SQW) structure consisting of a GaAs buffer layer, a 200nm-thick $Al_{0.3}Ga_{0.7}As$ barrier, a 10nm-thick GaAs quantum-well, a 50nm-thick $Al_{0.3}Ga_{0.7}As$ barrier, and a 5nm-thick GaAs cap layer was grown by molecular beam epitaxy (MBE) on a GaAs (001) substrate. A two-dimensional square lattice (~200nm window and ~800nm space) pattern with its edges parallel to the <100> and <010> directions was exposed on a polymethylmethacrylate (PMMA) resist film prepared on the SQW wafer using a JEOL JBX-5DII(U) EB lithography system operated at an accelerating voltage of 50KV. The resist pattern was developed by a mixture of methylisobuthylketone (MIBK):isoprophyl alcohol (IPA)=1:3 (20°C), and rinsed by IPA. Postbake was not undertaken in order to avoid a pattern degradation caused by the thermal flow of the resist at elevated temperatures.[14-15] Wet chemical pattern-transfer was performed by H_2SO_4-H_2O_2-H_2O system with a volume ratio of 3:20:10, which works as a reaction rate-limited etchant with an etch rate of 1.2mm/min at 0°C. Temperature of etchant was controlled by water bathing and the etchant was stirred to ensure the homogeneity of temperature and reaction species. Chemical erosion was stopped by deionized (DI) water flow. The PMMA was removed with boiled methylethylketone (MEK) after the DI water rinse. An $(NH_4)_2S_x$ treatment on QWBs was carried out at room temperature after the resist removal. PL measurements were performed before and after the $(NH_4)_2S_x$ passivation. Figure 3 shows a secondary electron image (SEI) of QWB array.

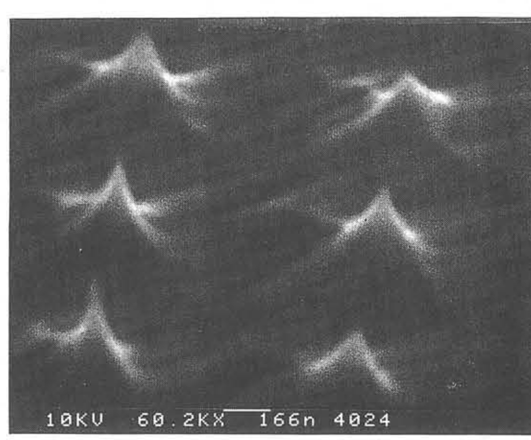

Fig. 3 SEI of GaAs/AlGaAs QWB array produced by processing a GaAs/AlGaAs single quantum-well (SQW).

3. Optical Properties

Figure 4 shows a typical example of PL spectrum from as-etched QWBs at 5.9K. It can be clearly seen that the PL peak of the QWB is blue-shifted from that of as-grown SQW by an amount of 11meV, from

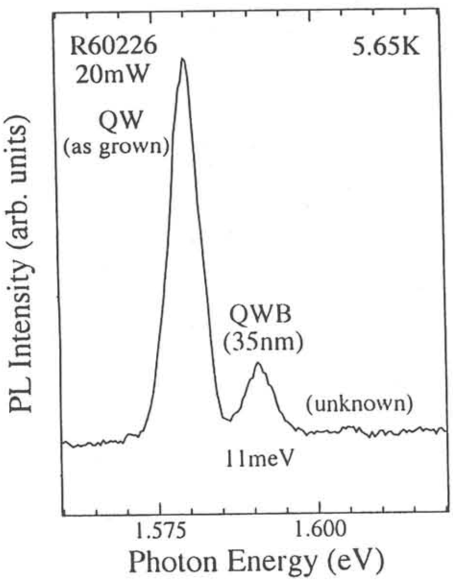

Fig. 4 PL spectra of QWB for various excitation powers (as etched).

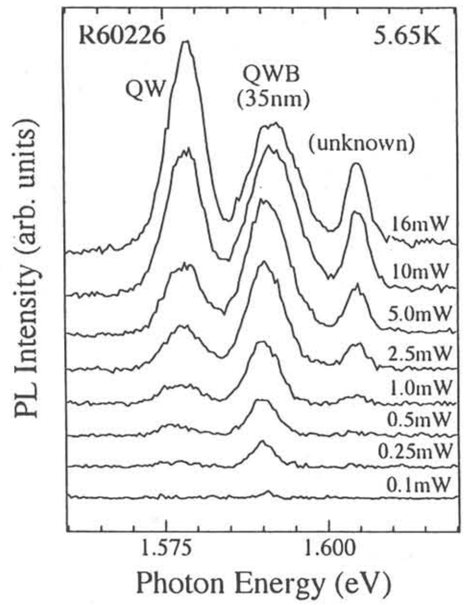

Fig. 5 PL spectra of QWB for various excitation powers (after passivation).

which the mean size of QWBs is estimated to be 35nm by a simplified analysis assuming a lateral confinement by an infinite barrier. To our knowledge, this is the first clear observation of blue shift due to three-dimensional quantum confinement in open GaAs/AlGaAs QWB structure.

We have also investigated the effect of sulfur treatment on the optical properties of QWBs. Shown in Fig. 5 is the PL spectrum of the same sample as that in Fig. 4 after the $(NH_4)_2S_x$ treatment. It can be seen in Fig. 5 that the PL intensity from QWB is enhanced as compared with that in Fig. 4; PL intensity for an excitation power (16mW) essentially equal to that in Fig. 4 (20mW) is increased and PL signal can be observed even in lower excitation powers down to 0.1mW. This indicates that the surface damage introduced through the chemical etching was reduced, which can be attributed to termination of dangling bonds by S atoms[16] and/or removal of the surface oxidized depletion layer, produced through the H_2SO_4-H_2O_2-H_2O process, by the $(NH_4)_2S_x$[17]. By virtue of the low damage wet etching combined with the $(NH_4)_2S_x$ treatment, PL from the QWB has been observed up to higher temperatures (27K). It can also be seen in Fig. 5 that a new PL line appears on the higher energy side of the QWB peak. At present the origin of the new line is not clear.

4. Conclusion

We have successfully fabricated GaAs/AlGaAs open box structures, which exhibit intense PL even in the quantum regime, by combining electron beam direct exposure and low-damage wet chemical etching. We have also shown that an $(NH_4)_2S_x$ treatment is effective in improving the optical properties of QWBs leading to a further enhancement of PL intensity.

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References

1) Y. Arakawa, H. Sakaki, Appl. Phys. Lett. **40**, 939 (1982).
2) T. Fukui, Appl Phys. Lett. **58**, 2018 (1991).
3) A. Madhukar, K. C. Rajkumar, P. Chen, Appl. Phys. Lett. **62**, 1547 (1993).
4) E. Kapon, S. Simhony, R. Bhat, D. M. Hwang, Appl. Phys. Lett. **55**, 2715 (1989).
5) S. Tsukamoto, Y. Nagamune, M. Nishioka, Y. Arakawa, J. Appl. Phys. **71**, 533 (1992).
6) B. E. Maile, A. Forchel, R. Germann, A. Menschig, H. P. Meier, D. Grutzmacher, J. Vac. Sci. Technol. **B6**, 2308 (1988).
7) S. R. Andrews, H. Arnot, P. K. Rees, T. M. Kerr, S. P. Beaumont, J. Appl. Phys. **67**, 3472 (1990).
8) A. Izreal, B. Sermage, J. Y. Marzin, A. Ougazzaden, R. Azoulay, J. Etrillard, V. Uhierry-Mieg, L. Henry, Appl. Phys, Lett. **56**, 830 (1990).
9) P. M. Petroff, A. C. Gossard, R. A. Logan, W. Wiegmann, Appl. Phys. Lett. **41**, 635 (1982).
10) M. Notomi, M. Naganuma, T. Nishida, T. Tamamura, H. Iwamura, S. Nojima, M. Okamoto, Appl. Phys. Lett. **58**, 720 (1991).
11) Y. Miyamoto, M. Cao, Y. Shingai, K. Furuya, Y. Suematsu, K. G. Ravikumar, Jpn. J. Appl. Phys. **26**, L225 (1987).
12) E. Ishikawa, S. Fukatsu, K. Onabe, Y. Shiraki, R. Ito, Proc. of IIAS Symposium on Science and Technology of Mesoscopic Structures, P-18, Nov. 6-8, 1991, Nara, Japan.
13) S. Iida, K. Ito, J. Electrochem. Soc. **118**, 118 (1971).
14) T. Katoh, Y. Nagamune, G. P. Li, S. Fukatsu, Y. Shiraki, R. Ito, Appl. Phys. Lett. **57**, 1212 (1990).
15) G. P. Li, T. Katoh, Y. Nagamune, S. Fukatsu, Y. Shiraki, R. Ito, Jpn.
J. Appl. Phys. **29**, L1213 (1990).
16) C. J. Sandroff, M. S. Hedge, L. A. Farrow, C. C. Chang, J. P. Harbison, Appl. Phys. Lett. **54**, 362 (1989).
17) H. Oigawa, J. Fan, Y. Nannichi, H. Sugahara, M. Oshima, Jpn. J. Appl. Phys. **30**, L322 (1991).