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Wide bandwidth lasing randomly assembled ZnS/ZnO biaxial nanobelt heterostructures

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Wide-bandwidth random lasing action is observed from the randomly assembled ZnS/ZnO biaxial nanobelt heterostructures under optical excitation. This is because optical gain at ultraviolet regime can be obtained from the near-band-edge radiative recombination of ZnS and ZnO. Surface defects related radiative recombination centers of ZnS and ZnO nanostructures also contribute to the visible optical gain. Hence, a broadband optical gain is obtained from the ZnS/ZnO biaxial nanobelt heterostructures. Moreover, a wide bandwidth coherent optical feedback can be achieved from the randomly assembled biaxial nanobelts due to high refractive index contrast between the nanobelts and air. © *2010 American Institute of Physics*. [doi:10.1063/1.3393997]

Conventional broadband and tunable multiwavelength semiconductor lasers and light-emitting diodes are usually realized by asymmetric multiple quantum well (QW) heterostructures (i.e., active region composes of QWs with different thickness) to provide optical gain over a wide bandwidth.[1,2] Recently, gain bandwidth of ~90 nm over the infrared regime has been demonstrated from the asymmetric multiple QW heterostructures.[3] Furthermore, the longitudinal band gap modulation of QWs has shown superluminescent of infrared radiation over a bandwidth of ~150 nm.[4] Nevertheless, the small band-offset energies of QW heterostructures, which are restricted by the lattice matching conditions at the interface between wells and barriers over a large surface area, limited the achievable gain bandwidth in infrared regime.

Recent development of nanotechnology has demonstrated the synthesis of heterostructured one-dimensional nanostructures from semiconductor materials with large lattice mismatch. For example, ZnO/ZnS nanocables can be fabricated in a two-step process utilizing the sulfidation of premade ZnS or oxidation of ZnO nanostructures.[5,6] Furthermore, ZnO nanobelt/ZnS nanowires heterostructures can be obtained through the epitaxial growth of ZnS nanowires onto ZnO nanobelts.[7] By thermal evaporation of ZnS powder in the presence of an Au nanoparticles catalyst, biaxial ZnO/ZnS nanoribbon heterostructures can also be realized.[8] As these heterostructures are composed of ZnS and ZnO, which have direct band gaps of 3.7 eV and 3.37 eV, respectively, a wide bandwidth luminescence over a ultraviolet (UV) regime should be possible. Furthermore, if random media can be formed by these heterostructures to support wide-bandwidth coherent optical feedback, broadband random lasing action should be obtained. In this paper, the possibility to realize random lasing action over a wide bandwidth from the randomly assembled ZnS/ZnO biaxial nanobelts is investigated.

A layer of randomly assembled ZnS/ZnO biaxial nanobelts were deposited on a Si substrate by a vapor transport method inside a horizontal tube furnace. Detailed fabrication procedures have been described elsewhere.[9] Figure 1(a) shows the x-ray diffraction (XRD) pattern of the as-grown sample, which XRD peaks are related to the hexagonal wurtzite (WZ) ZnO structure as well as WZ and cubic zinc blende structured ZnS. The field emission scanning electron microscopy image of the randomly assembled ZnS/ZnO biaxial nanobelts is shown in Fig. 1(b). The length of the nanobelts is ranging from 5 to 10 μm and the corresponding width is about 100 nm. The inset shows the corresponding high-magnification scanning electron microscopy (SEM) image. It is found that the nanobelts have a single-crystalline ZnS/ZnO biaxial heterostructure. Figure 1(c) shows the transmission electron microscopy (TEM) image of the biaxial nanobelts. A clear and uniform interface was observed along the nanobelt. High-resolution TEM image is also shown in Fig. 1(d), which illustrates that the nanobelt is

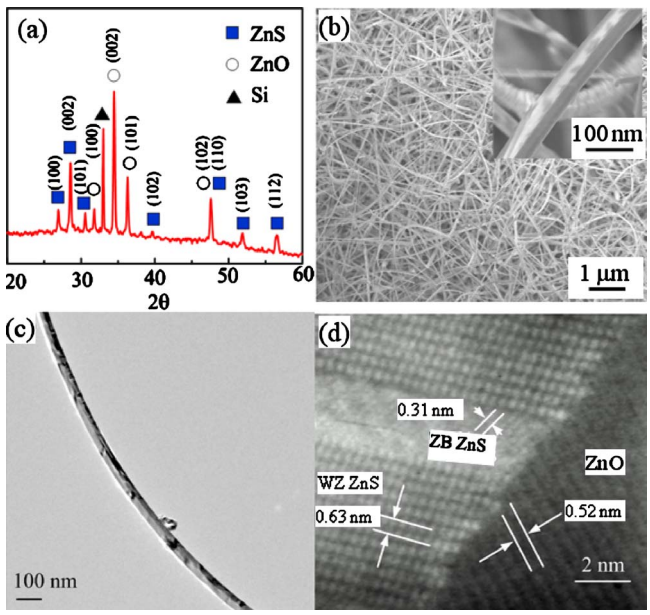

FIG. 1. (Color online) (a) XRD pattern, (b) Low-magnification SEM image, the inset shows the high-magnification SEM image, (c) TEM and (d) High-resolution TEM of the ZnS/ZnO biaxial nanobelt system.

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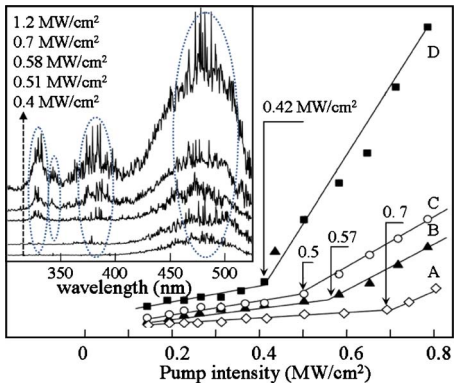

FIG. 2. (Color online) Light-light curves of ZnS/ZnO biaxial nanobelt heterostructures at different emission wavelength. The inset shows the corresponding emission spectra at different excitation power.

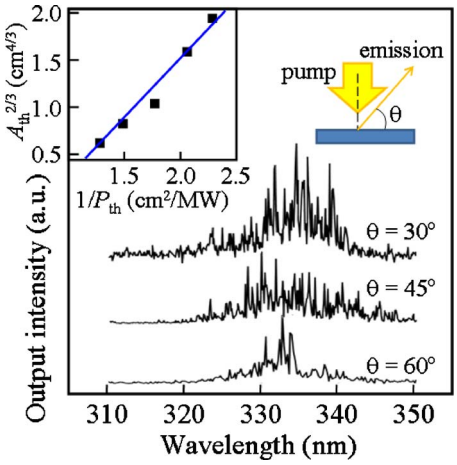

FIG. 3. (Color online) Emission spectra of the ZnS/ZnO biaxial nanobelt observed at different elevation angle, θ. The inset shows the relation between $A_{th}^{2/3}$ and P_{th}^{-1} for the cluster of ZnS/ZnO biaxial nanobelt.

composed of high-quality heterocrystalline ZnS and single-crystalline-ZnO crystal.

The sample was optically excited by a frequency-quadruplet 266 nm pulsed neodymium doped yttrium aluminum garnet (Nd:YAG) laser with 120 ps pulse-width and 10 Hz repetition rate.[10] A spherical lens was used to focus a pump beam of ~1 μm in diameter onto this sample's surface. Emission was collected from the edge of the sample. As shown in the inset of Fig. 2, when pumping intensities reached certain pump intensities, shape peaks with linewidth of ~0.4 nm started to emerge from the emission spectra. Further increase in pump intensities increases the number of sharp peaks. It can be shown that UV peaks emerged at around 332 nm are originated from band-to-band transitions of ZnS nanowires.[11,12] Furthermore, UV peaks at around 383 nm corresponds to the near-band-edge emission of ZnO nanowires. This is related to the radiative recombination of free-excitons through an exciton-exciton collision process.[7–9] Strong visible peaks are also detected at around 483 nm from the ZnS/ZnO biaxial nanobelts. These emission peaks are originated from either surface states of ZnS nanowires or singly ionized oxygen vacancy in ZnO nanostructures.[13,14] It is noted that the emission intensity of visible peaks is stronger than that of UV peaks. This is because a large amount of surface defect states, which is arisen from the large lattice mismatch between ZnS and ZnO, is induced by the large surface-to-volume ratio of the nanobelt heterostructure. Lasing peaks at around 355 nm, which has not been detected from either ZnO or ZnS nanostructures, was also excited at high excitation power. This is attributed to the presence of ZnS/ZnO heterostructure's interface.[9,15] Although the use of defect states to enhance radiative recombination is not preferred in bulk semiconductors, optical gain of nanostructured heterostructures can be extended from ultraviolet to visible wavelength. Therefore, the use of defect states seems to be an advantage in improving the optical characteristics of nanostructured semiconductors.

Figure 2 also plots the emission intensity of the ZnS/ZnO biaxial nanobelts at wavelengths around 332, 355, 383, and 483 nm versus pump intensities (i.e., light-light curves). It is noted that the lowest value of pump threshold, P_{th}, (i.e., sharp peaks are excited for pump intensity larger than P_{th}), which is equal to ~0.42 MW/cm^2, occurred at wavelength equal to ~483 nm. Value of P_{th} for the emission intensity at wavelength around ~383 nm (~332 nm) is ~0.5 MW/cm^2 (~0.57 MW/cm^2). The highest lasing threshold, which is equal to ~0.7 MW/cm^2, is detected at ~355 nm. These verified that the ZnS/ZnO biaxial nanobelts can provide high optical gain at wavelengths around 332, 355, 383, and 483 nm simultaneously.

From Fig. 1(b), it is noted that although the nanobelts are closely packed, air is filled in between the nanobelts. As the refractive index of ZnO (ZnS) nanobelts is about 2.1 (2.45), strong scattering strength can be obtained from the large refractive index contrast between nanobelts and air. Hence, it is possible to realize coherent optical feedback from the nanobelts over a wide range of wavelength. Scattering mean free path, l_s, of the randomly assembled nanobelts heterostructures over a range of wavelengths can be estimated by coherent back-scattering experiment using 405 and 473 nm ps laser diodes as the probe lights. It is estimated that l_s is about 0.8 times the wavelength of diode lasers. As l_s is less than the operating wavelengths, light may return to a scatter from which it was scattered before and thereby forming closed loop paths. This shows that the scattering strength of the randomly assembled nanobelt heterostructures is sufficient to achieve coherent optical feedback over a wide bandwidth.

In order to further investigate the lasing mechanism of the randomly assembled ZnS/ZnO biaxial nanobelts, Fig. 3 plots the emission spectra of the ZnS/ZnO biaxial nanobelts measured at different observation angles, θ. Different values of θ give different profile of emission spectrum. This is because different laser cavities formed by multiple scattering can have different emission directions. The inset of Fig. 3 shows the relation of threshold excitation area A_{th} and the pump threshold P_{th}. It is found that $A_{th}^{2/3}$ is roughly proportional to P_{th}^{-1}.[16] This implies that threshold conditions of the randomly assembled ZnS/ZnO biaxial nanobelts agree with the random laser theory.[17] Hence, it is verified that the lasing emission at ~332 nm is due to coherent random lasing action. Furthermore, it can be shown that the lasing characteristics of the randomly assembled ZnS/ZnO biaxial nanobelts at wavelength around 355, 383, and 483 nm are similar to that of 332 nm. The above experiments are consistent with our finding in ZnO thin films[16] so that the lasing mechanism of the four lasing wavelengths from ZnS/ZnO biaxial nanobelts should be related to coherent random laser action.

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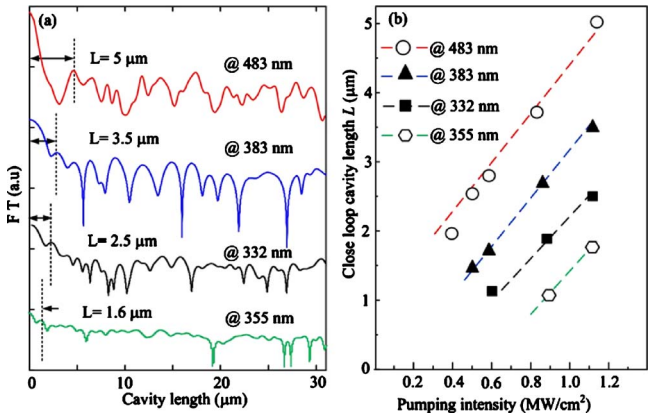

FIG. 4. (Color online) (a) Plot of FT of the lasing spectra of the randomly assembled ZnS/ZnO biaxial nanobelt centered at 483, 383, 332, and 355 nm. The arrow indicates the cavity length of the fundamental closed-loop cavity modes. (b) The variation in cavity length vs the pumping intensity of different emission wavelength.

As the lasing mechanism of the ZnS/ZnO biaxial nanobelt is due to coherent random laser action, it is also possible to deduce the cavity length of the corresponding closed-loop cavity modes by Fourier transform (FT).[10] Figure 4(a) plots the FT of the lasing spectra of the ZnS/ZnO biaxial nanobelts at emission wavelength centered at around 332, 355, 383, and 483 nm. The sample was pumped under an optical excitation of ~ 1.14 MW/cm^2 (i.e., 1.6 times the threshold for the lasing modes at wavelength around 355 nm). A series of broad peaks of harmonics, which corresponding to different cavity length of the random modes, are observed from the FT patterns. The closed-loop path length, L, of the fundamental cavity modes with lasing wavelength of 332 nm, 355 nm, 383 nm, and 483 nm are found to be ~ 2.5 μm, 1.6 μm, 3.5 μm, and 5 μm, respectively. This is expected if the lasing modes have the lowest P_{th}, the corresponding value of L will be the largest.[10,11] Fig. 4(b) plots the variation in L versus pump intensity for the lasing modes with wavelengths of $\sim$332, 344, 383, and 483 nm. It is observed that the value of L increases with the pump intensity for all the lasing modes. This is because the increase in pump intensity increases the optical gain of the random cavities. In this case, more closed loop random cavities are allowed to be formed inside the randomly assembled ZnS/ZnO biaxial nanobelts. Hence, it is required to increase the value of L in order to allow more closed loop random cavities to be formed.

In conclusion, wide bandwidth random lasing action has been achieved in randomly assembled ZnS/ZnO biaxial nanobelts under optical excitation. This is because the randomly assembled biaxial nanobelts provide optical gain and coherent optical feedback over a wide bandwidth for the formation of closed-loop random cavities. The optical gain at wavelength around 332 nm and 383 nm is due to the near-band-edge radiative recombination from ZnS and ZnO, respectively. Visible gain appear near 483 nm is arisen from either surface states of ZnS nanowires or singly ionized oxygen vacancy in ZnO nanostructures. A Zn–O–S ternary phase or an oxygen-doped ZnS nanostructure may be the reasons for the lasing emission centered at around 355 nm from the interface of ZnS/ZnO heterostructures. Furthermore, coherent optical feedback is achieved inside the randomly assembled biaxial nanobelts due to the high refractive index contrast between the biaxial nanobelts and air. Under optical excitation at room temperature, closed-loop random cavities over a wide bandwidth are excited and the corresponding size is dependent on its optical gain. The size difference of random cavities at visible and UV wavelength allows the simultaneous excitation of visible and UV random laser action from the ZnS/ZnO biaxial nanobelts.

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