Surface plasmon induced exciton redistribution in ZnCdO/ZnO coaxial multiquantum-well nanowires

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(Received 10 June 2010; accepted 28 July 2010; published online 24 August 2010)

The authors present the surface plasmon effects of Au nanoparticles on the photoluminescence properties of ZnCdO/ZnO coaxial multiquantum-well nanowires fabricated using chemical vapor deposition and pulse laser deposition methods. The spontaneous emission rate from ZnCdO quantum wells was increased by surface plasmon coupling by 1.29 times. The strong plasmon coupling between ZnO barriers and Au nanoparticles provides an extra fast decay channel for excitons generated in ZnO barrier layer and leads to exciton redistribution in ZnCdO/ZnO coaxial quantum wells, which promotes radiative recombination in ZnO barriers but reduces the number of excitons relaxing into the ZnCdO quantum wells. © *2010 American Institute of Physics*. [doi:10.1063/1.3480414]

Low-dimensional semiconductor oxides have attracted much attention in recent decade due to their potential applications and physical properties.[1,2] Among all the potential candidates, ZnO nanowire is considered to be a promising optical and electrical material for solar cells, gas sensors, field emission displays, UV lasers and solid state lighting, etc.[3–6] The band gap of ZnO can be readily tuned by alloying with Mg, Be, or Cd element to form ternary compounds.[7–10] High quality optoelectronic devices usually adopt a multiquantum-well (MQW) structure.[11] For one-dimensional coaxial quantum well wires, numerous reports on ZnMgO/ZnO based nanostructures have been published.[12] Recently, we have fabricated ZnCdO/ZnO coaxial multiquantum well nanowires (MQWNs).[13] To enhance spontaneous emission of light emitting materials surface plasmon (SP) coupling has been proven to be an effective way.[14–21] However, most of the related work focused on SP coupling with the semiconductor thin films or simple binary nanostructures such as ZnO nanowires.

In this letter, we present our investigation of SP effects on ZnCdO/ZnO MQWNs. Low temperature photoluminescence (PL) spectra were compared between the bare ZnCdO/ZnO MQWNs and Au nanoparticles (NP) capped MQWNs. The spontaneous emission rate from ZnCdO quantum wells was increased by SP coupling. The stronger SP coupling between ZnO and Au NP provides an extra fast decay channel for exciton generated in ZnO barrier layer and leads to exciton redistribution and distinct PL properties of the ZnCdO coaxial quantum wells.

The ZnCdO/ZnO MQWNs were fabricated on well aligned ZnO nanowires grown on GaN/sapphire substrates by chemical vapor deposition (CVD) method. An Au film of ~4 nm was first deposited on GaN/sapphires substrates by sputtering. ZnO and graphite powder (the weight ratio is 3:2) were grounded and loaded to an alumina boat. The details of fabrication process can be found in Ref. 11. Then the ZnO nanowire arrays were put into a pulse laser deposition (PLD) system. The ZnO and ZnCdO were alternatively deposited on the sample in order to form the coaxial MQWNs. The growth temperature and oxygen pressure in the chamber were maintained at 550 °C and 10 mTorr, respectively. The complete structure contains four QWs with 2 nm ZnCdO well layer and 3 nm ZnO barrier layer according to our thickness calibration result. The field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) and transmission electron microscope (TEM, JEM 2010F) were used to examine the morphology and microstructure of the MQWNs. For the PL measurement, a He–Cd laser (325 nm) was used as the excitation source. The PL signal was collected in a standard backscattering geometry and detected by a photomultiplier tube using standard lock-in technique. A close-cycled helium cryostat (Advanced Research System 4 K) was used to provide continuous temperature variation from 10 K to room temperature. For the time-resolved PL (TRPL) measurement, 325 nm laser pulses generated from an optical parametric amplifier which is pumped using a 150 fs, 1 kHz chirped-pulse amplifier were used to excite the samples. The time-resolved data were collected by an Optronis™ Optoscope streak camera system.

Figures 1(a) and 1(b) show the SEM images of the bare and Au NP capped ZnCdO/ZnO MQWNs. The average length and diameter of the nanowires are approximately 1 μm and 65 nm. After sputtering the Au NP, the morphology of nanowires becomes rough, which indicates that the Au NP have been capped and no continuous Au film is formed on the surface. Figure 1(c) is the TEM image of a single MQWN. From the figure, it can be clearly seen that the MQWN has smooth interface and surface. The total thickness of MQW is about 20 nm. Figure 1(d) is the high-resolution TEM image of a single MQWN.

PL spectra of the bare and Au NP capped MQWNs at 10 and 70 K are shown in Fig. 2. Besides the UV emission from the MQWNs, a broad emission band had also been found in the visible spectrum range which is commonly ascribed to emission from deep level defects[22,23] and will not be shown

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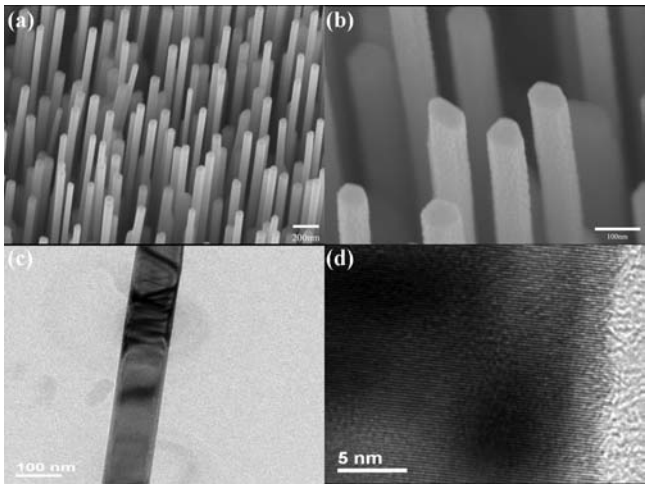

FIG. 1. [(a) and (b)] SEM images of bare and Au NP capped MQWNs. (c) TEM image of single MQWN. (d) High resolution TEM image of the MQWN.

here. At 10 K three obvious peaks can be identified at 3.371, 3.358, and 3.211 eV in the bare MQWNs. The first two bands can be assigned to the emissions from free exciton (FX) and neutral donor bound exciton (D^0X) of ZnO, while the emission at 3.211 eV is originated from the ZnCdO QW layers. With the temperature increasing, the relative intensity of FX emission of ZnO became stronger and D^0X merged with FX. The small peak which was indicated by the arrow in the inset and appeared at 70 K should be related to the first longitudinal optical phonon of FX. After sputtering the Au NP, the near band emission of ZnO was largely enhanced (about 35 times at 10 K) and the emission of ZnCdO decreased around 12 times. The inset of Fig. 2 shows the PL spectrum of Au NP capped MQWNs at 70 K. It is interesting to notice that after capping the Au NP the relative PL intensity of ZnCdO QW layers to the ZnO barriers is remarkably decreased. This result is very different from the previous report[15] in which the exciton-SP coupling largely enhanced the PL signal from the InGaN/GaN QW layer.

Figure 3 is the TRPL spectra taken at 10 K for the bare and Au NP capped MQWNs; around band edge emission

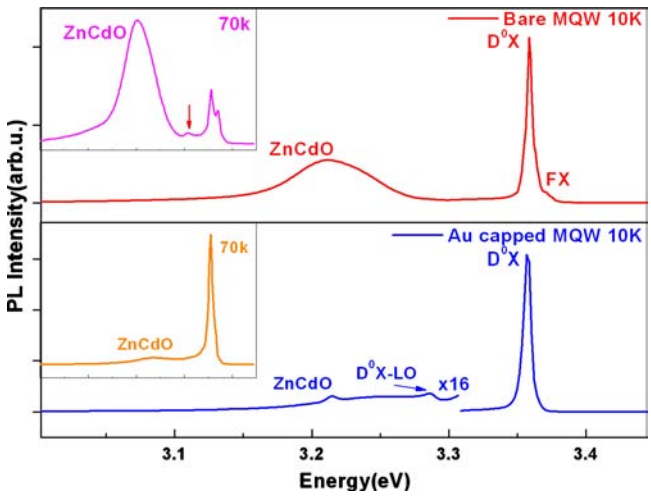

FIG. 2. (Color online) (a) Temperature dependent PL of the bare MQWNs. (b) The bare and Au NP capped MQWMs PL spectra at 10 K. The inset is the PL spectra at 70 K.

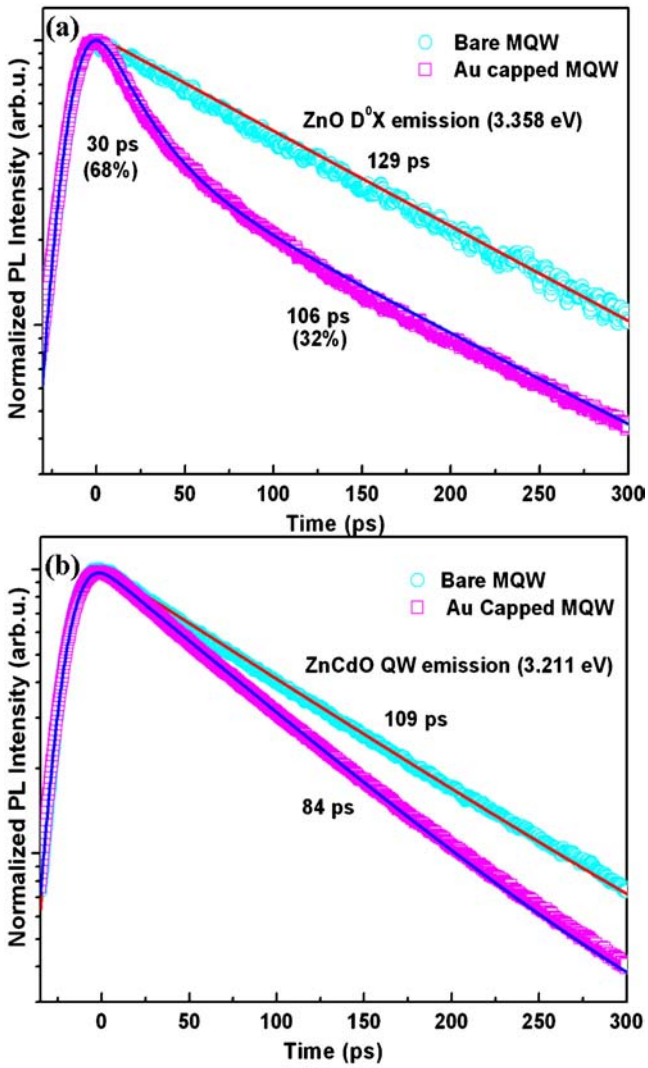

FIG. 3. (Color online) [(a) and (b)] Time-resolved PL spectra taken at 10 K for the bare and Au NP capped MQWNs: around band edge emission peak of ZnO and ZnCdO, respectively.

peak of ZnO [Fig. 3(a)] and ZnCdO [Fig. 3(b)], respectively. The instrument temporal response has been deconvolved from the fits. The D^0X PL decay of bare ZnO (taken from 3.348 to 3.369 eV) can be well fitted by a single exponential function. However, after sputtering the Au NP, there appears an extra short decay time about 30 ps for ZnO, which made up 68% of the whole decay life time. The strong coupling between SP and near band edge exciton of ZnO and fast Au NP SP oscillation relaxation process[24] should be responsible for this fast decay process. And the long life time, which made up 32% of the whole decay life time decreases from 129 to 106 ps. For the ZnCdO part, the PL decay can be fitted by a single exponential function. After capping the Au NP, the life time changes from 109 to 84 ps. It seems abnormal that the life time of ZnO is longer than that of ZnCdO for the bare MQWNs. This is probably because at low temperature the measured PL of ZnO originates from exciton bound to donor impurities and nonradiative recombination has little contribution to the decay. By comparing the extent of the life time change in ZnO and ZnCdO, it is found that the SP has a stronger coupling effect with the excitons in ZnO barrier, and especially the Au NP were directly capped on the outmost ZnO barrier layer, which we speculate will

result in exciton redistribution between barriers and QW layers. The Purcell enhancement factor was used to evaluate the enhancement of the spontaneous emission rate and can be calculated from the following equation, $F_p=(1/\tau^*/1/\tau)$, where τ and τ^* stand for the decay life time of bare and Au NP capped MQWNs. Using the TRPL data, we can get that the spontaneous emission rate was enhanced 1.29 times for ZnCdO active layer.

When the sample is excited by the laser, excitons will be generated in both the ZnO barriers and ZnCdO well layers, but exciton number generated in the barrier dominates. For the excitons generated in ZnO, some of them may recombine radiatively and the others will relax into the ZnCdO QW layer. At low temperature, excitons staying in ZnO are trapped by donor impurities and the PL is dominated by D^0X. As the temperature increasing excitons in the barriers get enough thermal energy to delocalize from the local potential dip and transfer into the ZnCdO wells. This should be the reason that the relative PL intensity from ZnCdO active layer gradually increases and even higher than the intensity of ZnO at around 70 K. After sputtering the Au NP, a large emission enhancement of ZnO and suppression of defect emission (spectra not shown here) have been found. For the suppression of defects emission, it has been reported that coating with dielectric materials can suppress the surface defects[25,26] and here the Au NP may have the similar effect. The analogous result has also been found in previously report.[20] Although the surface modification can reduce the probability of excitons trapped by defects and hence increasing the near band emission, the huge variation in PL intensity ratio between the ZnO and ZnCdO with and without Au NP cannot be ascribed to this process, because extra excitons also have opportunity to relax into ZnCdO QW to enlarge PL signal from it. We believe that exciton distribution has been changed by exciton-SP coupling in our system. After capping Au NP, the exciton generated in ZnO can strongly couple with SP of Au NP. So the excitons will have a bigger probability to radiatively recombine in the barriers. Accordingly, less excitons will relax into ZnCdO layers. Although the exciton-SP coupling in the ZnCdO layers can increase the spontaneous radiation rate, the reduction of exciton numbers in the wells leads to the decrease in the relative PL intensity from the ZnCdO. Therefore the strong coupling effect induces an exciton redistribution process in the MQWNs system, and should be responsible for the giant emission enhancement of ZnO instead of ZnCdO active layer.

In summary, the ZnO/ZnCdO MQWNs were fabricated through CVD and PLD methods. Besides reinforcing the emission of the active layer, a larger emission enhancement of ZnO barrier layer was obtained from the Au NP capped MQWNs. TRPL results indicate that spontaneous emission rates in ZnCdO wells were enhanced. The strong exciton-SP coupling effect in the barriers produces an extra fast decay channel and results in exciton redistribution between ZnO barrier layers and ZnCdO active layers. Our work suggests that rational integration of QWs and plasmonic structures is necessary to improve the emission efficiency in the QWs.

Supported from Singapore MOE under Grant No. RG40/07.

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