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A facile fabrication of Au nanoballs on ZnO shell Array based on nanosphere lithography for enhancement of optical properties

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Abstract

Noble metals nanoparticles (NMNPs) due to unique physical and chemical properties have attracted intense scientific interest for wide applications. Nanosphere lithography demonstrates a feasible strategy to achieve various metal nanostructures. In this paper, ZnO array is fabricated by magnetron sputtering method based on self-assemble polystyrene spheres (PSs) array. The thermal decomposition is used to achieve ZnO shell arrays by removing polystyrene spheres (PSs). The size of ZnO shell arrays can be controlled by changing the size of PS spheres. Disordered Au nanoballs coated on ZnO shell array are fabricated by electron beam deposition and the thermal decomposition to enhance optical properties of ZnO shell array. Optical properties, Morphology and chemical composition of Au nanoballs coated on ZnO shell array are analyzed by UV–vis Spectrophotometer, SEM and XRD. Based on localized surface plasmon resonance (LSPR) of the metal nanoparticles, the optical properties of ZnO shell array are enhanced by disordered Au nanoballs. Hence, it can be potentially applied in related optoelectronic devices.

Introduction

In recent years, noble metal nanoparticles (NMNPs) have attracted intense scientific interest due to unique physical and chemical properties for wide applications in surface-enhanced Raman scattering (SERS), structural color, bio-sensor, solar cells, Photoluminescence enhancement and photocatalysis [1–8]. This unique property is called as local surface plasmon resonance (LSPR) effect [9], which is resonant oscillations of their conduction band electrons at the metal surface during the interaction between NMNPs and lights [10]. Because of LSPR of NMNPs, they are used to improve light emitting properties of semiconductors, for example, ZnO and TiO2. Zinc oxide (ZnO) nanomaterial, as a low-cost and environmental material, has been regarded as one of the most promising candidates for various applications in light-emitting diodes, nano-generator, UV photodetectors and photocatalysts due to its wide direct band gap and high exciton binding energy [11, 12]. Hence, some works focused on enhancing the fluorescence efficiency of ZnO nanostructures by using different metal particles (Ag, Au, Al, Cu, and Pt) as capping layers [13–19]. For example, Yang group had reported surface Plasmon (SP) mediated emission of Ag/ZnO on different substrate. The result showed that the different substrates were found to be influential on the SP mediated light emission through metal films. The SP mode between Ag/ZnO and different substrate resulted in the emission enhancement or quenching [20]. Shan group found that the fluorescence of ZnO quantum dots (QDs) solution can be enhanced greatly by introducing carbon nanodots, meanwhile the lifetime of the fluorescence is decreased significantly due to the SP mode resulted in the emission enhancement or quenching [21]. In addition, they employed Ag nanoparticles to improve the emission characteristics of n-ZnO/i-ZnO/MgO/p-GaN structured light-emitting devices. The enhancement can be
attributed to the resonant coupling between the electron–hole pairs in the structure and the surface plasmons of the Ag nanoparticles [22]. However, the fabrication of these noble metals nanoparticles focused on chemical synthesis. In these methods, the coverage of nanoparticles is difficult to control because of the spontaneous aggregation of clusters. One of the great challenges in the fabrication of noble metal/semiconductor heterostructures is to synthesize composite structures rapidly and easily with no additive requirements. Creating controllable surface coverage of the nanoparticles is also important. In addition, H D Sun’s group used gold NPs-capped ZnO NRs to efficiently enhance the band edge emission and suppress the defect-related emission by combination of nanosphere lithography (NSL) and pulse-laser-induced annealing [23]. To some extent, these methods achieved large-scale fabrication and application of NMNPs on ZnO nanoshell array. Considering pulse-laser-induced annealing in the fabrication process, this was restricted to some extent.

In the work, large-scale disordered Au nanoballs coated on ZnO nanoshell array are fabricated by decomposing polymer polystyrene spheres based on nanosphere lithography. The size of ZnO nanoshell array can be regulated by choosing different diameter PS spheres. Large-scale disordered Au nanoballs coated on ZnO nanoshell array are achieved by magnetron sputtering and the thermal decomposition. LSPR effect of disordered Au nanoballs can enhance the absorption intensity of light to improve light emitting properties of semiconductors.

Methods and experimental

The disordered Au nanoballs coated on ZnO nanoshell array were fabricated by the NSL self-assembly process and thermal processing method [24]. Figures 1(a)–(j) shows 3D and side view of schematic illustration of fabricating Au nanoballs coated on ZnO nanoshell array. Firstly, the monolayer PS nanospheres (2.5 wt%) with the diameter of 200, 300, 400 and 500 nm were respectively self-assembled on clean ITO substrates by interface-assembly and transferred approach, as is showed in figures 1(a)–(b). And then, a ZnO layer with a thickness of 50 nm was deposited on the PS array at room temperature by radiofrequency (RF) magnetron sputtering (figures 1(c)–(d)). To achieve the ZnO nanoshell array (figures 1(e)–(f)), all samples were placed in annealing furnace. The annealing temperature is at 500 °C for 60 min to decompose the PS spheres. Then the ZnO nanoshell array was deposited with a 20-nm thick Au film using a standard electron beam deposition (EBD) system at normal incidence, as shown in figures 1(g)–(h). Finally, all samples were annealed in annealing furnace again. (The annealing temperature is at 500 °C for 60 min.). The disordered Au nanoballs formed on ZnO nanoshell array, as shown in figures 1(i)–(j). The morphologies and structure properties of the nanostructures were investigated using a field-emission scanning electron microscopy (FESEM) equipped with energy dispersive x-ray spectrum (EDS) analyzer. The x-ray diffraction (XRD) analysis of the nanoshell array was performed using a Rigaku/Max-2500 using Cu Ka radiation. Optical absorbance of all samples was examined by DU-88 UV–vis double-beam spectrophotometer. PL measurements were performed by excitation from a 325 nm line of a continuous-wave He–Cd laser.

Results and discussion

To prepare ZnO nanoshell array, the monolayer self-assemble PS spheres with different size used to the mask combined radiofrequency (RF) magnetron sputtering with the thermal decomposition. Figures 2(a)–(d) shows the SEM images of PS array with different diameter of 200 nm, 300 nm, 400 nm, and 500 nm respectively, which deposited with 50 nm ZnO film. It is obviously that ZnO nanoshell was obtained by annealing the PS spheres in the core at 500 °C in the annealing furnace for 60 min, and present hexagonal symmetry structures under the limitation of PS mask after annealing from the figures 2(a)–(d). In addition, there was the triangular gap between every three neighboring PS spheres. When the size of PS sphere is 200 nm, the triangular gap is about 20 ~ 30 nm, as is showed in figure 2(a). With increasing of the size of PS sphere, the triangular gap became bigger and bigger. When the size of PS sphere is 500 nm, the triangular gap is about 70 ~ 80 nm, as is showed in figure 2(d).

Large area disordered Au nanoballs on ZnO nanoshell array were prepared by annealing method. Figures 3(a)–(d) shows the SEM images with different magnification of disordered Au nanoballs on ZnO nanoshell array, which is prepared with 300 nm PS sphere. From figure 3(a), it is clearly seen that there are some Au nanoballs with different size attached to the gap between three neighboring ZnO nanoshells and the size of Au nanoballs is about 30 ~ 280 nm. However, there are some defects of point defect, line imperfection, which are caused by PS spheres self-assembly. To analyze carefully the variety of Au nanoballs after annealing, the SEM image of Au nanoballs on ZnO nanoshell structures are magnified further, as shown in figures 3(b)–(d). There are usually about four Au nanoballs around every ZnO nanoshell and one of these Au nanoballs is obviously bigger than others. The size of the biggest Au nanoball reaches nearly 280 nm, the other Au nanoballs varied...
from 40 nm to 120 nm. In addition, these nanoballs located at the triangular gap according to the minimum principle in energy, as shown in Figure 3(d). Some studies have shown that LSPRs are very sensitive to the size, shape, and dielectric around NMNPs. So, different size Au nanoparticles could provide more surface plasma resonance bands from the visible region to the near-infrared region. The annealing method can provide an effective one to fabricate different size Au nanoparticles. The averaging resonance effect of all Au nanoballs plays an important role in enhancing optical properties of ZnO nanoshells.

To contrast the size of Au nanoballs on different ZnO nanoshell array, PS masks with 200, 300, 400 and 500 nm respectively are used to prepare ZnO nanoshell array. Figures 4(a)–(d) show that the same Au film deposited on ZnO nanoshell array begins to melt and partially aggregates into Au nanoballs under thermal effects. It is seen that Au nanoballs on ZnO nanoshell array with 200 nm seem unordered and overlap due to surface roughness of ZnO nanoshell from figure 4(a). Moreover, it is difficult to differentiate ZnO nanoshell and Au nanoballs. It is verified that 500 °C temperature can induce the 20 nm Au film to melt, aggregate and form big Au nanoballs. When the size of PS sphere is 300 nm, Au nanoballs coated on ZnO nanoshells array seem slightly ordered compared with 200 nm ZnO nanoshell from figure 4(b). The main reason is that the size of big Au nanoballs approaches to 200 nm ZnO nanoshell, which caused them to be out of order. With increasing of the size of PS sphere, when the size of ZnO nanoshells increases to 400 nm, Au nanoballs coated on ZnO nanoshells became well-distributed, as shown in figure 4(c). To keep the lowest energy, aggregated Au nanoballs located at
the gap of three ZnO nanoshells. In addition, the size of Au nanoballs is matched with the gap. When the size of
ZnO nanoshells increased to 500 nm, Au nanoballs still located at the gap of three ZnO nanoshells. However, Au
nanoballs seem bigger than the ones coated on 400 nm ZnO nanoshells. During annealing, Au film coated on
500 nm ZnO nanoshells easily agglomerate together and form bigger Au nanoballs.

To further investigate the structure properties of the Au nanoballs coated on ZnO nanoshells, XRD and EDS
measurements were carried out. The XRD patterns of the Au nanoballs coated on ZnO nanoshells array are
shown in figure 5(f). On the sample, a dominant diffraction peak at 34.5° was characterized as the wurtzite ZnO
(002) diffraction, which indicates the preferential orientation along the wurtzite (002) direction in the ZnO
nanoshells. It should be noted that the peak located at 38.1° (2theta), corresponding to the Au (111) plane,
exhibits a stronger intensity in the Au nanoballs array. The XRD patterns show annealing temperature can affect
the crystal structure. At the same time, energy dispersive spectrum (EDS) patterns can evidence Au content and
ZnO crystal structure, as is showed in figures 5(b)–(e).
Optical property of ZnO nanoshell arrays, Au film coated ZnO nanoshell arrays and Au nanoballs coated on ZnO nanoshell arrays

Figure 6 shows the optical absorption spectra of PS array, ZnO nanoshell arrays and Au nanoballs coated on ZnO nanoshell arrays with 200, 300, 400 and 500 nm on ITO respectively. From Figure 6 (a), it is obviously seen that there is red-shift for absorption peaks of PS array. In addition, two absorption peaks appear at 390 nm and 476 nm respectively for 400 nm PS array. The absorption peaks of 500 nm PS array shift to 470 nm and 610 nm respectively. Previous results evidence that photonic band gap of PS array gradually red-shifted with increase of PS size [25]. Figure 6 (b) shows the optical absorption spectra of ZnO nanoshell arrays after removing PS. The position and intensity of absorption peaks of ZnO nanoshell arrays are significantly different from PS array. The absorption edge of ZnO nanoshell arrays red shift with the size of PS increasing. There is a wide absorption peak at 472 nm nearby for 200 nm ZnO nanoshell arrays, as shown in Figure 6 (b) (black line). When the size of ZnO nanoshell increased to 300 nm, a wide absorption peak red shift to 520 nm, and there is a very sharp peak at 395 nm nearby from Figure 6 (b) (red line). For 400 nm ZnO nanoshell arrays, the wide absorption peak red-shifts to 565 nm and a sharp, intensive absorption band appears at 448 nm nearby as shown in the blue line in Figure 6 (b). It would seem obvious that there are two obvious absorption bands at 430 nm and 541 nm nearby for 500 nm ZnO nanoshell arrays from the Figure 6 (b) (green line). The results show that ZnO nanoshell arrays have the outstanding optical band gap in the visible region and the optical band gap obviously red-shifts with increasing of the nanoshell size.

After Au film is deposited on ZnO nanoshell arrays, the absorption intensity is obviously improved compared with ZnO nanoshell arrays from the figure 6(c). The increasing size of Au nanoshell leads to broad LSPR peaks. For 500 nm PS sphere, LSPR peaks of Au film coated on ZnO nanoshell arrays red shift to near-infrared region. After annealing with 20 nm Au film coated on ZnO nanoshell arrays, some Au nanoballs attached to the interval of ZnO nanoshell arrays. Figure 6(c) shows the absorption spectra of Au nanoballs coated on ZnO nanoshell array using 200 nm, 300 nm, 400 nm and 500 nm PS spheres. It can be seen that the LSPR peaks shift from about 432 nm to 655 nm when the size of ZnO nanoshell increase from 200 nm to 500 nm. LSPR peaks of Au nanoballs coated on ZnO nanoshell arrays are obviously located at 440 nm and 523 nm. In addition, there are some broad LSPR peaks at 508 ∼ 665 nm for 500 nm Au nanoball coated on ZnO nanoshell arrays.

Figure 7 shows PL spectra of ZnO nanoshell arrays, Au film coated on ZnO nanoshell arrays and Au nanoballs coated on ZnO nanoshell arrays using 300 nm spheres. PL spectra show that PL peak of ZnO nanoshell arrays is at 540 nm, the PL spectra of Au film coated ZnO nanoshell arrays is at 625 nm and the PL peak of Au nanoballs coated on ZnO nanoshell arrays is at 590 nm. It shows that the luminescence intensity increased by about 4 times in Au nanoballs coated on ZnO nanoshell arrays, the size and density of Au nanoballs are the key factors to influence the luminescence intensity. When Au nanoparticles interacted with ZnO nanoshell array, the SP energy of Au nanoparticles can also be scattered and reemitted into effective free space radiation. In this case, the radiative decay rate of ZnO can be raised effectively, leading to the PL enhancement [25].
Conclusion

Large-scale disordered Au nanoballs coated on ZnO nanoshell array are fabricated by decomposing polymer polystyrene spheres based on nanosphere lithography. ZnO nanoshell array can be regulated by choosing different size of PS spheres from 200 nm to 500 nm. In addition, the thermal decomposition can provide an...
effective method to fabricate different size Au nanoballs on ZnO nanoshell array without other chemical. The size of Au nanoballs varied from 20 nm to 280 nm. These Au nanoparticles exhibit more LSPR band for enhancing optical absorption. These novel metal nanostructures have potential wide applications in surface enhanced Raman scattering (SERS), photocatalysis, solar cells, nonlinear optics and single molecule detection.

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