3D PLASMINIC NANOARCHITECTURES

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Keywords: 3D, Plasmonics, ZnO, Dewetting.

Abstract
In this work, we report a 3D nanoplasmonic platform which is achieved by a dewetting process of an Au thin film deposited on the surface of zinc oxide (ZnO) nanorods. Vertically aligned ZnO nanorods are fabricated by the epitaxial growth on a gallium nitride (GaN) substrate. An Au thin film is then evaporated on the ZnO nanorods, and dewetted Au nanoparticles are finally self-assembled on the ZnO nanorods via an annealing process. Depending on the thickness of the Au thin film, the diameter of dewetted Au nanoparticles was changed, which led to a shift of localized surface plasmon resonance (LSPR). We further found that the number of dewetted Au nanoparticles on top of the ZnO nanorods increased with the top area, but it did not show a linear relationship. Our fabrication approach based on a dewetting process would offer tunable 3D nanoplasmonic platforms for next-generation plasmonic optical devices.

1 Introduction
Plasmonic nanostructures with a localized surface plasmon resonance (LSPR), which is generated by the coupling of light to the collective oscillation of electrons on the nano-sized metallic surface, have generated considerable interest with the development of nanotechnology due to its ability to enhance the weak physical process such as the absorption of light.[1] By adopting such a plasmonic nanostructure inside/onto/beneath a photoactive layer, a power conversion efficiency of solar cells could be improved because an electromagnetic (EM) field is greatly enhanced by plasmonic "hot spots".[2] Furthermore, optical biosensors such as surface-enhanced Raman scattering (SERS) could be designed with an ultrahigh sensitivity through a local field enhancement from the "hot spots".[3] A variety of optoelectronic devices and optical biosensors integrated with plasmonic nanostructures thus have been explosively studied and developed.
Metallic nanoparticles using gold (Au) or silver (Ag) have been widely used to create plasmonic active layers (i.e. "hot spots") in the integrated devices due to the ability to easily tune the plasmon resonance frequencies by changing their material, size, and arrangement.[4] However, those plasmonic layers usually using nanoparticles with about 50 nm in a diameter form two-dimensional (2D) plasmonic domain, so that it has a big limitation that optical active layers (e.g. a photoactive layer) with a thickness of over 100 nm are not sufficiently enhanced because plasmonic enhancement only has an effect in the vicinity of plasmonic nanoparticles (see Figure 1a). To overcome such confined plasmonic effects in a 2D

plasmonic layer, three-dimensional (3D) plasmonic nanostructures could be suggested for expanding plasmonic effects to the entire range of optical active layers, as shown in Figure 1b. Previously, some works have shown interesting 3D plasmonic nanostructures by coating a metal on nanowires or nanorods, but they also have a problem that it is difficult to control the dimensions and the resonance frequencies of plasmonic nanostructures according to the purpose of their applications. It is therefore essential to develop a new strategy for creating tunable 3D plasmonic nanostructures via a high-throughput and effective fabrication.
In this work, we report a 3D nanoplasmonic platform which is achieved by a dewetting process of an Au thin film deposited on the surface of zinc oxide (ZnO) nanorods. Vertically aligned ZnO nanorods are fabricated by the epitaxial growth on a gallium nitride (GaN) substrate. An Au thin film is then evaporated on the ZnO nanorods, and dewetted Au nanoparticles are finally self-assembled on the ZnO nanorods via an annealing process. Depending on the thickness of the Au thin film, the diameter of dewetted Au nanoparticles is tuned, which lead to a shift of LSPR. We further investigate the relationship between the number of dewetted Au nanoparticles and the top area of ZnO nanorods. Our fabrication approach based on a dewetting process would offer promising 3D nanoplasmonic platforms for next-generation plasmonic optical devices.

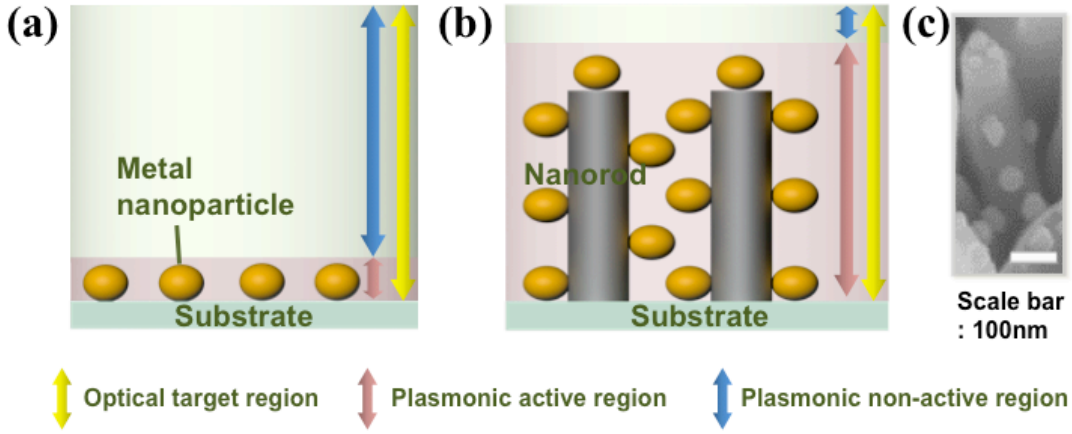

Figure 1. Comparison of plasmonic effect region in 2D and 3D nanostructures. Metal nanoparticles (a) on a planar substrate and (b) on top and on the sides of nanorods. (c) SEM image of 3D plasmonic nanostructures by dewetting a metal thin film on nanorods.

2 Materials and testing methods

As mentioned above, 2D plasmonic nanoparticle array only affects a part of an optical active layer, as shown in Figure 1a. However, 3D plasmonic nanostructures as shown in Figure 1b can provide plasmonic enhancement to most of optical active layer. As a result, they can effectively lead to the enhancement of device performance such as energy conversion efficiency in optoelectronics or sensitivity in optical biosensors. We could achieve the 3D plasmonic nanostructures by dewetting a metal thin film on nanorods, where the dewetted nanoparticles were formed on both the side and the top of a nanorod as shown in Figure 1c. The detail mechanism and process will be presented later in this article.
Figure 2 shows ZnO nanorods epitaxially-grown on a gallium nitride (GaN) substrate. Undoped GaN epilayers with 4μm thickness were prepared by metal organic chemical vapor deposition (MOCVD) on c-form aluminum oxide (c-Al_2O_3) substrate and the Au thin layer (2 nm) was deposited on GaN epilayers to use a catalyst for the synthesis of vertically aligned ZnO nanorods, and then the ZnO nanorods arrays were grown at 880° for 2 hr.[5] In order to form metal nanoparticles on the surface of the ZnO nanorods, an Au thin film was first prepared on ZnO nanorods by a thermal evaporation. By annealing the Au-deposited ZnO

nanorods at 650 °C for 3hr, the dewetted Au nanoparticles were successfully self-assembled on the surface of ZnO nanorods (see Figure 3). Since the dewetting process is simple and low cost, our fabrication approach could provide a high-throughput and cost-effective process in a wide range and over large areas. Even though we used vertically aligned ZnO nanorods, different shapes and materials as a nanorods template could be applied. Furthermore, we performed the dewetting process for 3 hr at 650°C using 20-nm-thick Au deposited nanorods, but dewetting time, temperature, and deposited material and its thickness are critical parameters to form nanoparticle size and position. Thus, the 3D plasmonic nanostructures with a various morphologies and properties could be realized by controlling their dewetting parameters and nanorods template.

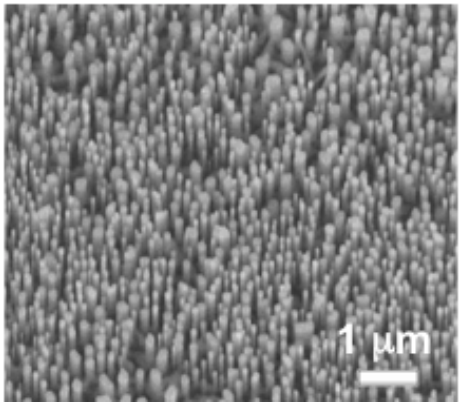

Figure 2. ZnO nanorods on GaN prepared by epitaxial-growth.

We prepared two kinds of Au deposited ZnO nanorods and their thicknesses are respectively 10 nm and 20 nm. The mean diameters of dewetted Au nanoparticles on the surface of ZnO nanorods were respectively 36 nm and 52 nm. The diameter of the dewetted Au nanoparticles increased as the thickness of the deposited Au film increased. In case of metal nanoparticles, confined conduction electrons oscillate in resonance with the electromagnetic field leading to localized surface plasmons and their plasmon resonance frequency depends on their size and position.[6] In other words, since the size of dewetted nanoparticles can be easily tuned by controlling the thickness of Au film deposited on the nanorods, the plasmon resonance frequency could be controlled for the purpose of their applications. In order to confirm the optical properties according to the size of the dewetted Au nanoparticles on the surface of ZnO nanorods, we measured the optical absorption spectra of the 3D plasmonic nanostructures. For the 10 nm Au-deposited nanorods, the plasmon resonance peak is clearly observed at about 534 nm after annealing, and dewetting for the 20 nm Au-deposited film yields the resonance peak at about 572 nm. They have various size and interparticle distance of nanoparticles, the control of which can cause plasmon resonance peak shift. The main morphological difference between the nanostructures annealed for the 10 nm and 20 nm films is the size of the dewetted Au nanoparticles. The size of the nanoparticles increases as the thickness of deposited Au film increases. Consequently, the red-shift of plasmon resonance peak has been observed with increasing dewetted nanoparticle size, and this tendency is similar to the previous results of 2D plasmonic nanostrcutures.

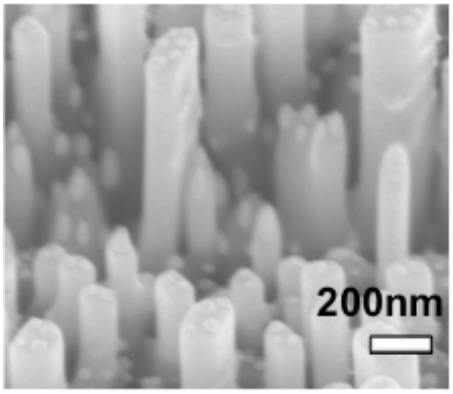

Figure 3. Dewetted Au nanoparticles on ZnO nanorods.

3. Conclusions

We have developed plasmonic nanostructures that could enhance the plasmonic effect in a three-dimensional region by dewetting a metal on the surface of nanorods. Because the dewetted metal nanoparticles could be discretely placed on the surface of the nanorods, it is anticipated not only to expand the plasmonic effect to the entire range of optical active layer for optoelectronics, but also to improve a sensitivity to detect target moledules for optical biosensors due to the increased plasmonic surface area. Furthermore, we found that the plasmon resonance frequency can be easily controlled by tuning the thickness of the deposited metal film, and these results may enable 3D plasmonic nanostructures to be designed for the purpose of their applications. Thus, our strategy may provide a wide range of opportunities for optoelectronics, such as OSC and OLED, and optical biosensors to enhance their performance.

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