Probing Sub-5 nm Gap Plasmon Using Collapsible Nano-fingers

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Plasmonic nanostructures are of great interests recently due to their ability to concentrate light to small volume. They have many potential applications in optical communication, disease diagnosis, and chemical sensing. Therefore it is extremely important to investigate the plasmonic hot spots both theoretically and experimentally. While it is theoretically predicted that the optimal hot spot is a sub-5 nm gap between two metallic particles [1], due to the difficulties in fabrication of sub-5 nm structures, most of the studies on hot spot behaviors at that scale are either theoretical only or based on collective behaviors of multiple hot spots (i.e. dense-packed nano-particles separated by spacers) which do not necessarily behave the same as each individual hot spot. Therefore, it is essential to find a way to fabricate hot spots with sub-5 nm gap sizes deterministically and reliably as the experimental platform to probe and utilize those hot spots.

Recently, we have successfully fabricated gap plasmonic structure with precisely controlled nano-gap by using collapsible nano-fingers [2, 3, 4]. The fabrication process is summarized in Figure 1. First, a nano-finger array in flexible polymer (i.e. nanoimprint resist) is fabricated using nanoimprint lithography (NIL), and metallic caps, such as gold disks, are deposited on the top of each finger using electron-beam evaporation. Second, atomic-layer deposition (ALD) is used to coat a thin conformal dielectric layer. Finally, the nano-finger sample is dipped into Ethanol (water works too) and air-dried. When the Ethanol dries up, the capillary force makes the nano-fingers close together. The ALD-coated dielectric layer serves as the spacer to define the gaps between the metallic particles. If we use TiO2 as an example, each atomic layer of TiO2 is only about 1Å thick, which means the gap between the metallic particles can be precisely controlled with an accuracy of 2 Å and as small as 2 Å. For the first time, we can reliably achieve such small gaps deterministically and precisely. It is the ideal experimental platform to probe the rich sciences at the gap plasmonic hot spots.

Figure 2 shows the SEM images of the collapsible nano-fingers before and after collapse. The nano-fingers collapsed uniformly. The ALD TiO_2 layer in this sample is about 2 nm thick, and therefore the gap between two gold disks is defined as 4 nm after two fingers close and contact each other. However, the TiO_2 is too thin to be observed under SEM.

As the polarized light shone on the dimer-like structure, it will trigger dipole-like charge distribution inside gold nanoparticle. Based on classical electromagnetic theory, field at gap center increases as the gap gets smaller. However, as gap size reduces, for sub-5 nm gap structure, electron tunneling between two gold nanoparticles becomes significant, which would cancel part of the charge in opposite sides and hence reduce the field. The competing factors result in an optimal gap size for the strongest optical field enhancement. But such a small gap structure has not been fabricated reliably until recently we demonstrated how to define and scale sub-5nm gaps by using collapsible nano-fingers.

As shown in Figure 3, the absorption spectra of the collapsed nano-fingers using TiO2 as gap material have been characterized, which reveal how this tunneling effect can tune the plasmonic enhancement at hot spot. In the first time, we determine the optimal gap size experimentally from the spectra. Furthermore, in order to control the tunneling strength, we also used different gap dielectric material which can provide different tunneling barrier height and therefore tune the tunneling strength, as shown in Figure 4. As Al_2O_3 has slightly higher tunneling barrier than TiO_2 (0.16 eV higher), it has an optimal gap size smaller than TiO_2. Because HfO_2 and SiO_2 have small electron affinity, which means even higher tunneling barrier, both of them have smaller tunneling effect, resulting in an optimal gap less than 0.8 nm that cannot be shown in the spectra..

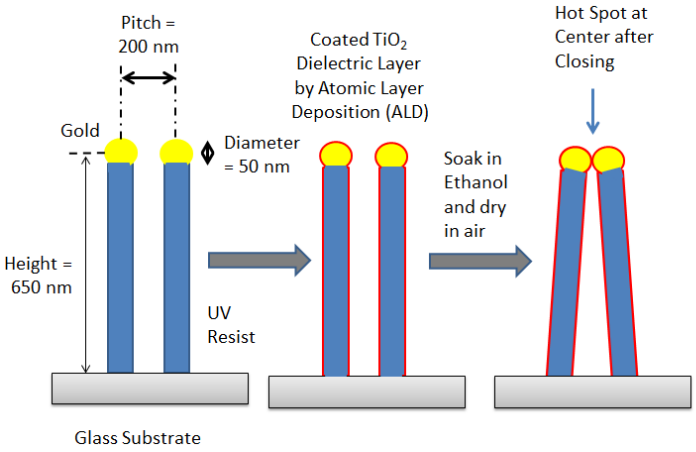


Figure 1. Schematic of controllable hot spots created using nano-fingers.

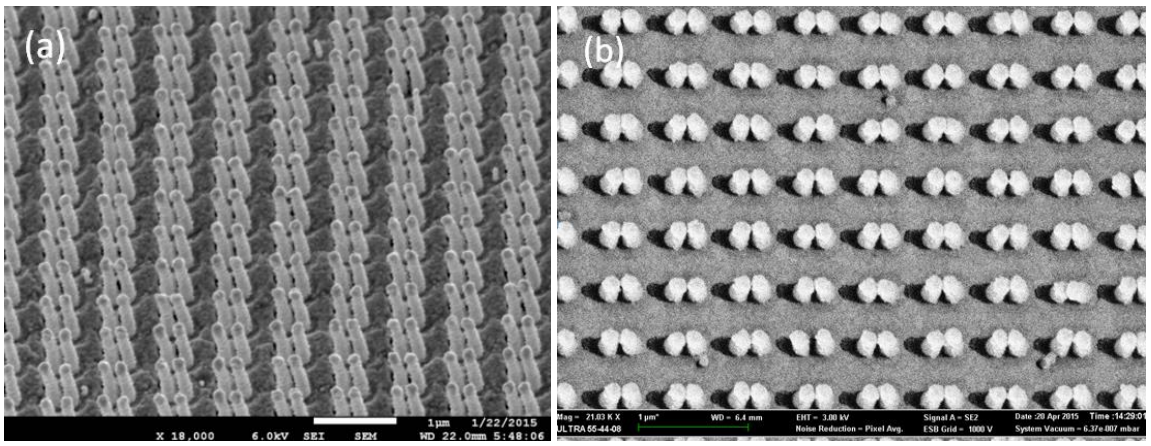
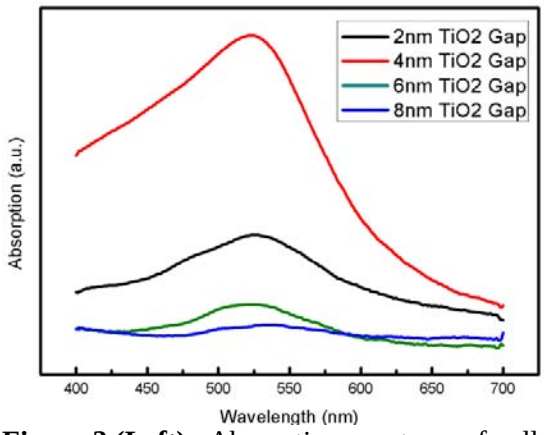


Figure 2. SEM images of collapsible nano-fingers: (a) before collapse (b) after collapse (The ALD TiO_2 layer is about 2 nm thick, which cannot be observed under SEM)



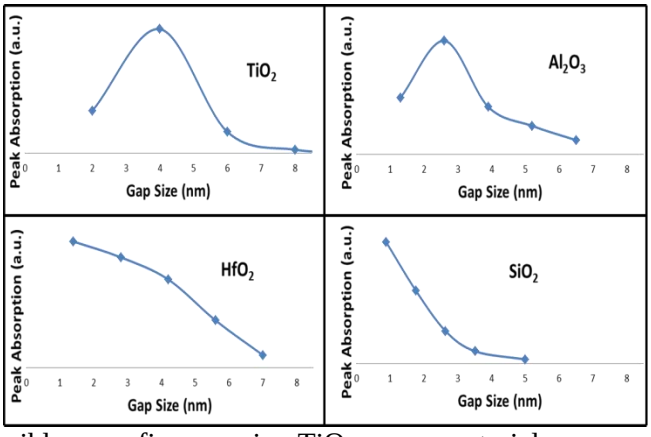


Figure 3 (Left). Absorption spectrum of collapsible nano-fingers using TiO_2 as gap material
Figure 4 (Right). Peak absorption strength vs. gap size for different gap material

References

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