Highly Tunable Surface Plasmons Using Metal/metal Oxide Hybrid Nanostructures

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ABSTRACT

Metal and metal oxide electrodes have gained lots of interest in many optoelectronic devices including photovoltaics, light emitting diodes, sensors, batteries and biophotonics . In light harvesting devices, one dimensional electrodes increase surface area which in turn enhannces the light absorption, charge transfer and charge collection effieincies. A novel nanoimprint lithography method is used to fabricate nanostructured electrodes (NSEs). Silicon mold is used to imprint nanostructures with different dimensions and geomerties . The polymer film is then cured at ~ 150 °C to fabricate nanostructures. Large area nanostructured hybrid silver and transparent conductive oxides (TCOs) including ITO and IZO arrays with feature sizes below 100 nm have been fabricated. The optical and electrical properties of these core shell electrodes including the surface plasmon frequency can be tuned by suitably changing the dielectrics and their dimensions. The surface plasmon wavelength of the nanopillar Ag changes from 650nm to 690nm depending on the dimensions of the pillars. Adding layers of ITO to the structure shifts the resonance wavelength toward the infrared region by an amount depending on the sequence and thickness of the layers in the structure.

Keywords: nanostruture, core shell, plasmonic, Transparent Conductive Oxide

1 INTRODUCTION

Interests in patterning polymer based nanodevices and creating sub-100nm metal and TCO based NSEs have led us to modify traditional imprinting lithography technique enabling synthesis of an array of sub-30nm diameter polymer nanostructures. In this approach, a hard e-beam lithographed Si or SiC master is used to directly imprint a large area nanopattern onto polyacrylonitrile (PAN) film. The PAN film is then cured at ~ 200 °C to synthesize nanostructures. Metal and metal oxide based TCOs can then be coated with different thickness onto the PAN structures to create the electrode nano structures. Details of the fabrication process can be found in reference 1[1]. PAN nanostructured scaffold is stable under most of the metal / metal oxide deposition conditions and provides a unique flexibility of synthesizing composite electrodes with stacked layers of different dielectrics. However, PAN being a weak dielectric modification of the electronic properties in the nanostructured TCOs (or single dielectric) is not significant. In this paper we report fabrication of several scalable Ag and TCO based core-shell NSEs with alternate Ag / TCO and SiO2 / Ag concentric rings, the dependence of their electrical and optical properties on the nanostructure dimensions. Although SiO2 core gold shell type nanoparticles have been explored in detail for their nanoscale optical properties, such structures including traditional TCO materials have never been studied before, in particular in relation to tuning electrical properties suitable for fabrication of organic photovoltaic systems.

2 ELECTROD FABRICATION

ITO nanostructured electrodes of 1cm × 1cm area were fabricated by depositing ITO via electron beam deposition technique[2]. The nanopillars are with diameter of 170 ± 8.8 nm and height of 442 ± 10.6 nm; the error is the width at half maximum in the Gaussian dispersion profile computed using ImageJ. The center-to-center pitch in this structure was 200 ± 2.4 nm resulting in an average wall-to-wall distance of ~15nm. A large area top view and cross-section scanning electron microscope (SEM) image of nanostructured ITO (NSITO) is shown in Fig. 1A. This structure was created by depositing 150nm ITO onto PAN nanopillars resulting in 30nm thick coating on the sidewalls and 150nm coating on top of the pillars and plain region at the base of the pillars.

3 RESULTS AND DISCUSSION

The surface area in the NSITO in Fig. 1A is up to 9 times larger than the plain ITO. large surface area is mostly due to the sidewall region of the nanopillars. More details on surface area enhancement factor in different nanostructured electrodes can be found elsewhere.[3] Figure 1 B shows transmission and reflection spectra of plain and nanostructured ITO. Transmission of nanostructured ITO is higher than planar counterpart while its reflection is lower. The optical band edge of NSITO is red shifted. In addition to bulk optical bandgap a second smaller optical band gap ~3.25 eVis observed in NSITO. Note that bulk optical band gapsvalues of 3.4 to 3.7 eV have been reported in literature [4].

Optical and electrical properties of nanostructured electrodes differ from their planar counterparts. A SEM image of Ag nanopillars is shown in figure 2b. Figure 2a shows absorption spectra of the sample.As one can see within particular wavelength range nanostructured sample shows less absorption (higher transmission) relative to planar one. Due to surface plasmon excitation at the interface of Ag with air, electric filed enhances at particular

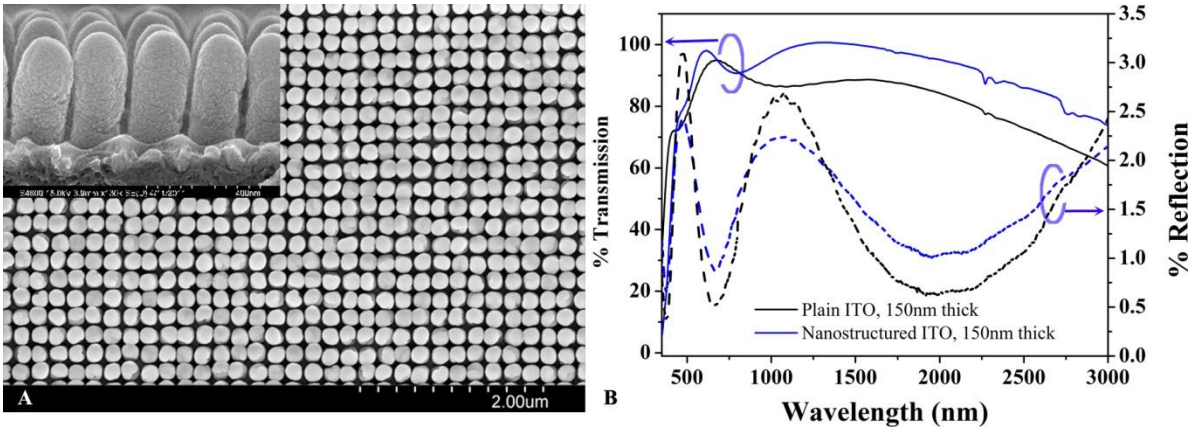
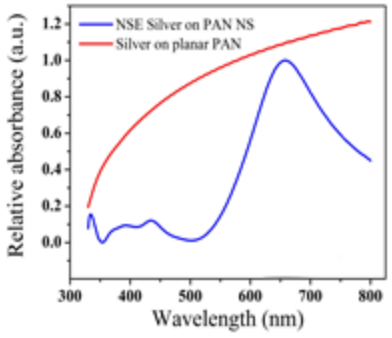


Fig.1 A. Scanning electron microscope image of a nanostructure polymer core ITO shell electrode with diameter of 170 ± 8.8 nm and height of 442 ± 10.6 nm; inset shows the cross section image of the nanopillars. B. Comparison of transmission (solid line) and reflection (dashed line) spectra between 150nm thick plain and nanostructured ITO electrodes.

wavelength which is dependent on the dimensions of the pillar. At shorter wavelength (300-500 nm) relative to plasma wavelength (650 nm here) nanostructured Ag electrod is more transparent.Surface plasmons of Ag nanopillars couple to free space and each other. Dimensions of the nanopillars including diameter, length and pitch (center to center distance) can be optimize to obtain maximum transmission at desirable wavelength region. Due to electric filed enhancement and hence large intensity of the electric field, plasmonic electrods can be used as an effiecient substrate for Surface Enhanced Raman Scattering(SERS)[5]. Raman enhancement factor of up to 10^6 was obtained using Ag pillars shown in figure 2a. Ag nanopillars with different dimensions show different absorption peaks . As the aspect ratio of the pillars increases absorption redshifts which is in agreement with FDTD simulation. Ag nanopillars with surface area enhancement factor of up to 13 has been fabricated. Resistivity of the electrod changes from 2 to 0.5 Ω/□ for planar sample.

Recently we have shown that the optical band gap can be fine tuned by changing the shell thickness on the sidewall. NSITO also shows lower specular reflection and calculated carrier concentration is ~ 5 – 6 times larger than the flat ITO sample and a strong function of the shell thickness.

Metals such as Au and Ag have large free carrier concentration. Surface plasmon propagation and frequency of surface plasmon excitation is direcly relative to carrier concentration. Since Ag has larger free carrier concentration than Au, its plasma frequency is in shorter wavelength (uv region of spectrum) while Au shows plasmonic behavior in visible range. ITO and other highly doped transparent conductive oxides have large free carrier concentration however its less than Ag and Au; thus plasma frequency in TCOs is shifted to IR .Doping



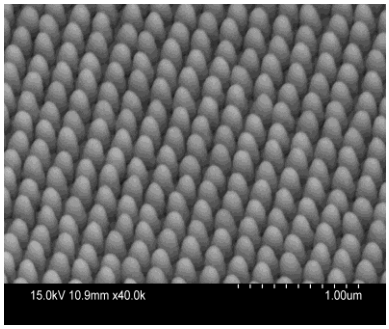


Figure 2 a) absorption spectrum of 50 nm Ag deposited on the pillars. b) side view of Ag deposited on PAN

concentration and ratio have direct impact on plasma wavelength and can be optimized to tune the plasma excitation.

To further investigate the role of dielectrics on the optical properties of the nano structured electrodes we developed an array of electrodes with traditional SiO2 / Ag multi-layer configuration within the nanorods in different

orders. Expectedly the optical characteristics of these electrodes are strong functions of geometry of the layers and surrounding dielectrics and can be explained using traditional hybrid plasmonic model based on Drude model. Detailed FDTD modeling confirmed the experimental results and preliminary results indicate that by changing the layer dielectrics optical and electrical properties can be modified.

Devices with ITO (70nm)/Ag (10nm)/ITO (70nm) structure are also fabricated. Complete elipsometry spectroscopy is described elsewhere[6]. There is an absorption peak around 430 nm which is attributed to Ag nanoparticles. Charge distribution around short axis of Ag nanopillars which is along the pillars top view cross section induces short wavelength absorption peak. Different charge distribution along the height of the pillars causes a red shift in the absorption. Plasmon hybridization between Ag shell and dielectric embedding or core medium creats plasmon frequencies in shorter and longer wavelenghts.

Resistivity of nanostructured ITO scales up with surface area. Electrodes with larger surface area show resistivity of 1800 Ω/□. Depositing a very thin layer of Ag in different configuration reduces the resistivity dramatically. Resistivity values down to 65 Ω/□ is obtained. Thickness and sequence of intermediate Ag layer can be optimized to achieve good conductivity and transparency. With increasing conductivity, free carrier concentration increases hich in turn induces more absorption and less transparency in the electrodes.

4 CONCLUSION

We show that the optical and electrical properties of metal and metal oxides can be modified in a new generation of nanostructured electrodes with core shell geometry. By changing the dielectric medium, geometry, thickness and separation between the nanostructures, the key optical and electrical parameters, such as, band gap, carrier concentration and resistivity can be fine tuned to suit device requirements.

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