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Optical properties of ZnO/Au core/shell nano-tips

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1. Introduction

One-dimensional ZnO nanostructures, such as nano-wires, nano-rods, and nano-tips, have attracted a growing interest in photovoltaic applications to enhance the light harvesting efficiency due to the wide band gap energy, direct charge transport path way, and large surface area [1]. However, the dye sensitized solar cells based on ZnO nanostructures have a limitation that the aggregate crystals produced by the instability between ZnO surface and acidic dye degrade the device performance. In order to overcome this problem, the ZnO nanostructures coated by TiO_2, Al_2O_3, and SiO_2 have achieved the improved stability against acidic dye solution [2-4]. Recently, there have been several efforts to improve the optical absorption efficiency by employing the surface plasmon in metal nano-structures [5]. In this presentation, we fabricated the Au-deposited ZnO nano-tips (NTs) by thermal evaporation because the Au exhibits excellent stability against acid solution. Moreover, Au has a good capacity to enhance the light absorption. The specially designed nanostructures (ZnO/Au core/shell NTs) could enhance significantly the optical absorption.

2. Experimental results and Discussion

Figure 1 shows the schematic diagram of the fabrication process for ZnO/Au core/shell nano-tips (NTs) on 650 nm F-doped SnO_2 (FTO) as transparent conduction oxide layer (TCO) coated on soda-lime glass substrates. For the synthesis of ZnO NTs by a hydrothermal method, the 5 nm ZnO seed layer was deposited on FTO coated glass substrate by a RF magnetron sputtering at room temperature. Then, the ZnO seed layer deposited on FTO coated glass was dipped into zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.9% purity) and hexamethylentetramine (HMT, $C_6H_{12}N_4$, 99.9% purity) aqueous solution under constant stirring at a gradually decreased temperature from 98 ^oC to 75 ^oC for 10 hours for highly tapered ZnO NTs and then dried on the hot plate of 60 ^oC. In order to fabricate ZnO/Au core/shell NTs, hydrothermally grown ZnO NTs were deposited with Au by thermal evaporation for 400 s at 0.05 nm/s deposition rate.

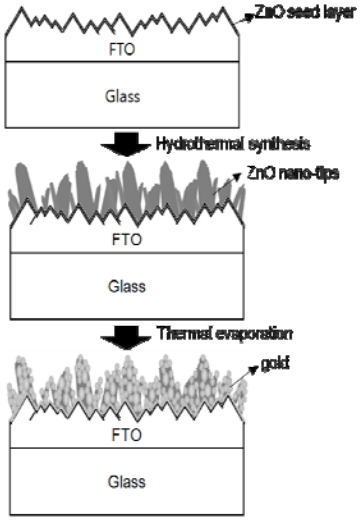

Fig. 1. Schematic diagram of ZnO/Au core/shell NTs process.

Figure 2 shows the cross section and top-view field emission scanning electron microscope (FE-SEM) images of (a) 650 nm FTO coated glass, (b) 400 s Au-deposited FTO coated glass, (c) ZnO NTs on FTO coated glass, and (d) 400 s Au-deposited ZnO NTs (ZnO/Au core/shell NTs) on FTO coated glass. As shown in Fig. 2(a), the average thickness of FTO film is 650 nm and the FTO coated glass has a rough surface. Therefore, the ZnO NTs were diagonally aligned along the surface of FTO film as shown in Fig. 2(c). The density of ZnO NTs was relatively high in 0.01 M zinc nitrate concentration. The height and size of ZnO NTs were 100-350 nm and 15-100 nm, respectively. As shown in Fig. 2(d), it is obvious that ZnO NTs were well deposited with Au by thermal evaporation in comparison with uncoated ZnO NTs in Fig. 2(c). It is expected that ZnO/Au

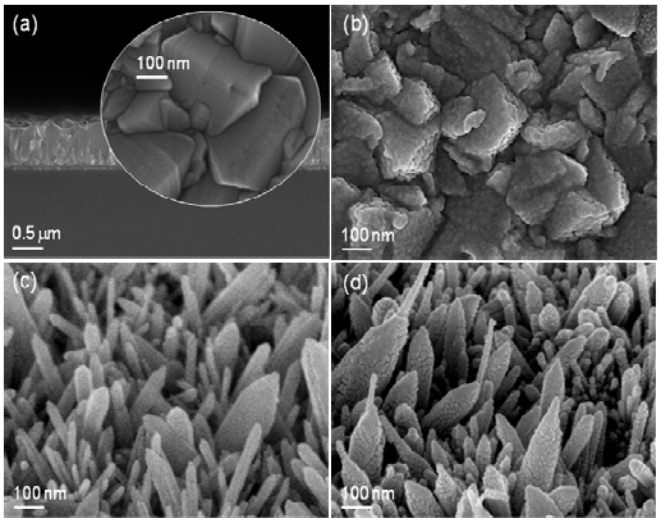

Fig. 2. Cross section and top view FE-SEM images of (a) 650 nm FTO coated glass, (b) 400 s Au-deposited FTO coated glass, (c) ZnO NTs on FTO coated glass, and (d) ZnO/Au core/shell NTs on FTO coated glass.

core/shell NTs can improve the stability against acidic dye solution in ZnO based dye sensitized solar cells (DSSCs).

Figure 3 shows the measured absorption spectra of FTO coated glass, ZnO NTs on FTO coated glass, Au-deposited FTO coated glass, and ZnO/Au core/shell NTs on FTO coated glass in the wavelength range of 0.3-1 μm. The absorption characteristics were obtained by $A(\lambda) = 1-T(\lambda)-R(\lambda)$. Here the transmittance and reflectance spectra were measured by a Cary 5000 UV-Vis-NIR spectrophotometer in diffusion mode.

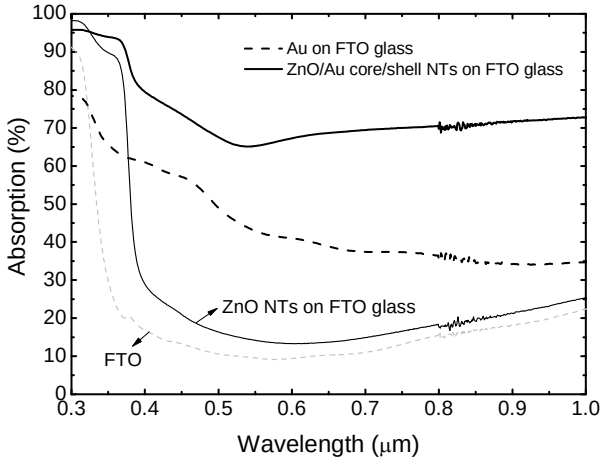

Fig. 3. Measured absorption spectra of FTO coated glass, ZnO NTs on FTO coated glass, Au-deposited FTO coated glass, and ZnO/Au core/shell NTs on FTO coated glass.

As shown in Fig. 3, the FTO coated glass has a low absorption spectra < 12% from 0.47 μm to 0.73 μm. As the ZnO NTs was grown on FTO coated glass, the absorption was slightly increased from 0.45 μm to 1 μm and dramatically increased in higher incident light energy region than ZnO band gap energy (3.3 eV, i.e., 0.375 μm). When the ZnO NTs were deposited with Au by thermal evaporation, however, the significantly enhanced light absorption of > 65% was observed over a wide wavelength range of 0.3-1 μm. This can be explained by efficient Au surface plasmon effects. Also, in the case of Au-deposited FTO coated glass, the absorption was significantly increased than that in FTO coated glass for the same reason. However, in comparison of Au-deposited FTO coated glass and ZnO/Au core/shell NTs, the absorption of ZnO/Au core/shell NTs is considerably enhanced than that of Au-deposited FTO coated glass. This means that the Au surface plasmon on ZnO/Au core/shell NTs can be efficiently enhanced due to large Au-deposited surface area of ZnO NTs and antireflection effects.

Figure 4 shows the measured diffuse reflectance spectra of Au-deposited FTO coated glass and ZnO/Au core/shell NTs on FTO coated glass. As shown in Fig. 4, the ZnO/Au core/shell NTs significantly reduce the reflectance because NTs structures have an efficient refractive index profile for antireflection [7]. As results, the absorption of ZnO/Au core/shell NTs can be considerably improved due to the efficiently enhanced surface plasmon effects.

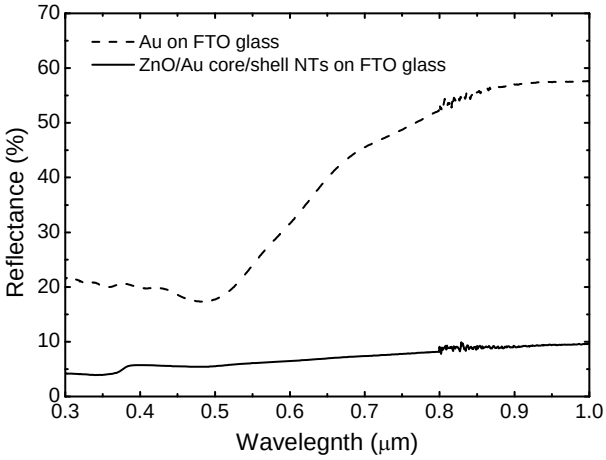

Fig. 4 Measured reflectance spectra of Au-deposited FTO coated glass and ZnO/Au core/shell NTs on FTO coated glass.

3. Conclusion

The ZnO/Au core/shell NTs can be promising hybrid nano-structures to be stable against acidic dye solution in ZnO based DSSCs as well as to significantly enhance optical absorption. The improved light absorption of ZnO/Au core/shell NTs is due to large Au-deposited surface area of ZnO NTs and anti-reflection effects caused by the efficiently enhanced surface plasmon effects.

Acknowledgements

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