論 文 内 容 の 要 旨

Recent years, ZnO nanostructures have attracted much more interest to be used as photo electrode in DSSC application. Comparing to traditional dye-sensitized solar cells (DSSCs) photo electrode material TiO2, ZnO not only has wide bandgap energy of 3.37eV, but also has much higher electron mobility (up to 1000 cm2 /V s). However, the development of dye-sensitized solar cells has reached bottleneck in the improvement of efficiency. One reason is difficult to obtain textured TiO2 with large surface area to absorb more dye molecules.

In order to increase surface area of photo electrodes for dye absorption, we designed a novel dye-sensitized solar cell structure to try to achieve large surface ZnO nanorods to replace TiO2. In this dissertation, my main work focused on the fabrication of vertical well-aligned large surface ZnO nanostructures for dye-sensitized solar cell applications. There were three main requirements for ZnO nanostructures to be used in dye-sensitized solar cell applications: (a) The suitable substrates (b) Vertical well-aligned ZnO nanostructures with large size; (c) large surface area.

Based on our previous work, I did the original novel research to meet these requirements, mainly three parts: (a) high transmittance and conductivity ITO substrates for the DSSCs; (b) developing novel multi-annealing technique to fabricate large size vertical well-aligned ZnO nanostructures; (c) firstly introducing the novel mist chemical vapor deposition (Mist CVD) technique to regrow and modify the vertical well-aligned ZnO nanostructures.

1. High transmittance and conductivity ITO substrates for the DSSCs

The popular substrate materials for DSSC are TCO substrates, such as ITO, FTO, AZO, etc. Comparing to FTO and AZO, the ITO, also having higher transparence, conductivity and binding strength, especial it is much easier to be fabricated, are good alternatively substrate materials for DSSC applications.

In my research, ITO films were fabricated in our lab. The influences of the ITO film thickness (100nm~500nm) on the properties of ITO films and ZnO nanostructures fabricated on the ITO substrates were investigated. The roughness, resistivity and Hall mobility of ITO films increased with the increase of film thickness. The density and alignment of ZnO nanostructures gradually increased with the ITO film thickness decreased. ZnO nanostructures formed by reducing annealing method on 300nm-thickness ITO substrate showed the highest density and alignment. Therefore, 300nm-thickness ITO film is the optimized substrate for the DSSCs applications.

2. Novel multi-reducing annealing technique

Our previous work had succeeded in obtaining the hexagonal-cone ZnO nanostructures on ZnO film using low-temperature treatment in a reducing gas ambient on the quartz glass substrate. But the ZnO nanostructures needed be vertical well-aligned and also grown on the ITO substrates. Therefore, I developed a novel multi-reducing annealing technique to fabricate vertical well-aligned ZnO nanostructures with large size on the ITO substrates.

The effects of annealing parameters including the temperature and time on the properties on vertical well-aligned ZnO nanostructures were investigated.

Vertical well-aligned ZnO nanostructures were fabricated with different annealing temperature and time in reducing gas. With the increase of annealing temperature, the size and aspect ratio of ZnO nanostructure increased due to the increase of the growth speed. With the extending of annealing time, ZnO nanostructures would firstly be grown up and then etched due to the gradual exhaustion of the oxygen in the furnace.

The effects of different annealing processes including the pre-annealing, the reducing/oxygen annealing time ratio on the properties of vertical well-aligned ZnO nanostructures were investigated.

The pre-annealing process was firstly introduced to treat the ZnO films at low-temperature in forming gas ambient. The pre-annealing process could etch the surface of ZnO films, help obtaining more Zn nuclei before the grownup of ZnO nanostructures. The influences of pre-annealing temperature and time on the growth of ZnO nanostructures were investigated. The results indicated the optimized pre-annealing process was annealing in 300°C for 3h in forming gas.

The reducing/oxygen annealing time ratio was an important parameter in the multi-annealing technique. The influence of reducing/oxygen annealing time ratio on the growth of ZnO nanostructures was investigated. The results indicated the reduced zinc atoms from films will react with oxygen to contribute ZnO nanostructures regrowth if suitable oxygen was supplied to the ZnO films. But if excess oxygen was supplied to the ZnO films, the growth of ZnO nanostructures would be suppressed. Therefore, optimized multi-annealing process with suitable reducing/oxygen annealing time ratio (2:1), transferred zinc atoms from ZnO film to ZnO nanostructures, resulting in the ZnO nanostructures growing remarkably.

With the optimization of the multi-annealing processes, the vertical well-aligned ZnO nanostructures with large size were fabricated on the 300nm-thickness ITO substrates. The ZnO nanostructures with uniform hexagonal head with diameter of 300 nm and average height of 2500 nm were formed after multi-annealing processes. In the range of visible wavelength, ZnO nanostructures on ITO substrates showed a relatively high transmittance (>70%).

3. Novel mist chemical vapor deposition technique

The novel mist chemical vapor deposition technique was developed to fabricate oxide material films at the beginning. I firstly introduced this novel technique to be used to regrow the nanostructures and modify the surface morphology.

In order to obtain large surface area in the ZnO nanostructures, the vertical well-aligned ZnO nanostructures were treated by a novel mist chemical vapor deposition system. The size and morphology of ZnO nanostructures could be controlled well by optimizing Mist CVD treatment parameters.

The influences of treatment time and carrier gas were investigated. The size of ZnO nanostructures increased with the increase of treatment time. With the Mist CVD treatment time extended, the surface morphology of ZnO nanostructures were modified with covering intertwined nanosheets on the surface, which significantly increased the surface area of the ZnO nanostructures.

The crystallinity of ZnO nanostructures was significantly dependent on the carrier gases. If the carrier gas was Argon, the obtained ZnO nanostructures exhibited good single crystal. If the carrier gas was oxygen, the obtained ZnO nanostructures showed polycrystalline. The growth mechanism of ZnO nanostructures in Mist CVD treatment was investigated.

Vertical well-aligned ZnO nanostructures with large surface area were fabricated via the mist chemical vapor deposition with suitable time and carrier gas, the size of ZnO nanostructures was extended to 1350nm and 3500nm in the diameter and average height, respectively.

Additionally, the growth mechanism of the ZnO nanostructure by the multi-annealing method was investigated. The fabrication and modification methods of ZnO films and ZnO nanostructures were investigated. The working principles, apparatus structures and parameters, and operation processes of fabrication equipment and characterization devices were studied during my Ph.D. thesis.

At last, the demonstrated ZnO-based DSSCs were fabricated with ZnO nanostructures on ITO substrates as photo anode. The effects of the size and density of ZnO nanostructures were investigated. The results indicated that the high density and large size were contributed to the high efficiency of DSSC due to the increase of the dye absorption. The best overall conversion efficiency we already obtained was about 3.65% with a fill factor 0.528.