論 文 の 内 容 の 要 旨

論文題目　Efficient photoanode made of ZnO-metaloxynitride core-shell nanowire array on a film for hydrogen generation by photocatalytic water splitting
(光触媒的水分解による水素発生のためのZnO-金属酸窒化物コア-シェル型ナノワイヤアレイ膜を用いた高効率光アノードに関する研究)

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Hydrogen is an efficient carbon-free energy carrier, offering several advantages over fossil fuels such as a high energy density of about 120 MJ/Kg, no greenhouse gases emission and clean by product after delivering energy by thermal or electrochemical combustion with oxygen. Many research efforts have been made to develop an efficient and sustainable way for hydrogen generation. Compared to the conventional hydrogen generation by fossil fuel consumed processes of electrolysis and steam reformation of natural gases, hydrogen generation by photoelectrochemical (PEC) water splitting cells using solar radiation is essentially clean. However, two major issues, namely, stability and efficiency, of the PEC water splitting cells still remain challenging. The stability of PEC water splitting cells is determined by the photo-anticorrosive ability of the electrodes, and thus electrodes made of photo-anticorrosive materials are necessary. On the other hand, the efficiency of PEC water splitting cells has been limited by the electrode performance in absorbing light, separating charges and transporting carriers.

To address these limitations, nanostructured photoelectrodes made of one-dimensional semiconductor nanowire array on a conductive film are expected to enable superior performances over their film counterparts. First, the nanowire array realizes an anti-reflection surface to increase the light absorption. Second, the nanowire array gives large surface areas that enhance chemical reaction for water decomposition. Finally, the diameters of the nanowires are in nanoscale,

and thus reduce the carrier diffusion length in the diameter directions of the nanowires leading to improved charge separation at the nanowire surface areas to support an enhanced chemical reaction of water decomposition. Therefore, the fabrication of functional semiconductor nanowire array structure is important. However, single semiconductor material does not simultaneously fulfill all the requirements, say good chemical stability, strong light absorption property, suitable energy band position and easy fabrication of functional nanostructures. To this end, the composite core-shell nanowire heterostructures consisting of two semiconductor materials are proposed in my research to satisfy those requirements for stable and efficient PEC water splitting.

In the first part of my research, a nanowires-on-a-film structure consisting of dense and vertically aligned ZnO nanowires on a ZnO film was synthesized using *a*-plane sapphire as a substrate and Au nanoparticles as growth catalysts through a one-step chemical vapor deposition (CVD) process. This simple CVD process enables the growth of a dense ZnO nanowire arrays on a ZnO film in the wurtzite phase with a single domain texture and highly oriented along the ZnO *c*-axis direction over large areas. This result is evidenced from the systematic studies of the crystal texture quality of the ZnO nanowires-on-a-film sample by scanning transmission electron microscopy, selected area electron diffraction technique, X-ray θ-2θ scan, diffraction pole figure and rocking curve analyses.

The epitaxial mechanism of the single-domain texture and hightly *c*-oriented ZnO nanowire array on a ZnO film structure was further elucidated. A single-crystalline $ZnAl_2O_4$ buffer layer was formed between the epi-ZnO film and the *a*-plane sapphire substrate. The single crystal and well oriented $ZnAl_2O_4$ buffer layer (with aligned crystallographic orientations of the Al_2O_3 [11-20] parallel to the $ZnAl_2O_4$ [0-21] and parallel to the ZnO [0001]) provides an improved in-plane symmetry, reduces lattice mismatches and therefore favors the epitaxial growth of the high-quality ZnO nanowire on a ZnO film structure. The elucidated role of the $ZnAl_2O_4$ buffer layer in supporting the epitaxial growth of the ZnO nanowires and the ZnO film on the *a*-plane sapphire may have a profound impact on the growth techniques of single-domain and highly *c*-oriented ZnO films and nanostructures.

Moreover, the growth mechanism of the ZnO nanowires and the ZnO film is clarified by the CVD study of growing the ZnO nanowires and ZnO film using different amount of Au catalysts. It is evidenced that the length of the fabricated ZnO nanowires largely increases with the increased amount of Au catalysts and thus the one-dimensional ZnO nanowires is very likely grown by a Au-sacrificial VLS growth

process. In comparison, the growth of ZnO film is very likely governed by a vapour-solid (VS) process, since the thickness of the film has a "saturated" value of ~ 2 μm when the amount of Au used is more than 1 nm for the CVD growth. With the understanding of the epitaxial and growth mechanism of the ZnO nanowires and ZnO film, the large-scale and homogeneous fabrication of the ZnO nanowires-on-a-flim structure composed of vertically aligned ZnO nanowires having different lengths on a thick ZnO film has been achieved.

The optical and electronic properties of the ZnO nanowire array on a ZnO film structure under the growth condition of 2 nm Au catalyst were characterized by the low-temperature photoluminescence (PL) spectroscopy and electrochemical impedance spectroscopy. Free exciton and bound exciton emissions along with the phonon replica emissions were clearly observed in the low-temperature PL spectrum, indicating a good optical property and a high crystalline quality of the fabricated ZnO nanowire arrays on a ZnO film structure. An n-type semiconductor behaviour and the carrier density of ~ 10^{17} cm^{-3} were obtained from the electrochemical impedance analysis of the ZnO nanowire array on a film sample.

In the second part of my research, a dense ZnO-$ZnGa_2O_4$ core-shell nanowire array on a film structure was synthesized using the fabricated ZnO nanowires-on-a-film samples as the substrates in the second-step CVD process. The process realizes a homogeneous growth of the core-shell nanowires over a large area on the substrate and enables the electrical contact of the core-shell nanowires through their underneath film of the same material.

The ZnO cores and $ZnGa_2O_4$ shells of the core-shell nanowires are of single crystal quality and have aligned crystallographic orientations of the ZnO cores [0001] parallel with the $ZnGa_2O_4$ shells [111] as evidenced from XRD θ-2θ and transmission electron microscopy (TEM) analyses. The ultraviolet-visible diffuse reflectance analyses showed two sharp near-band-edge absorptions of the ZnO cores and the $ZnGa_2O_4$ shells. This reconfirms the core-shell nanowire structure. In addition, the electrochemical impedance analyses and photocurrent-voltage scan were used to identify the flatband potential, carrier density and interface band bending of the ZnO-$ZnGa_2O_4$ core-shell nanowire array samples. An n-type semiconductor property, a flat-band potential of ~ -0.4 V (versus NHE) and a carrier density of ~ 10^{19} cm^{-3} were obtained for the ZnO-$ZnGa_2O_4$ core-shell nanowires. Compared to the ZnO nanowires, the enhanced cathodic flatband potential of the ZnO-$ZnGa_2O_4$ core-shell nanowire array provides a more suitable energy band position for the water splitting chemical reaction. Also, the increased carrier density of the

core-shell nanowire array samples improves the conductivity, leading to a possible reduction of the ohmic energy loss in the PEC cell circuit. The amperometric study of the ZnO-$ZnGa_2O_4$ core-shell nanowire array sample showed clear on-off current cycles with switching on and off the light illumination. A very low current density less than 10^{-4} mA/cm^2 was obtained in the dark condition, while a stable and large photocurrent density of 1.2 mA/cm^2 was obtained with a bias of 1.23 V_{RHE} under a 300 W Xenon lamp illumination. This stable photocurrent observed under the continuous light illumination reveals that the $ZnGa_2O_4$ shells worked as an anti-corrosive outer-layer of the ZnO nanowires and enhanced the stability of the photoanode in contrast to the ZnO or n-doped ZnO nanowires whose PEC performances can be deteriorated under the light illumination.

In the third part of my research, a nitridation process was carried out on the ZnO-$ZnGa_2O_4$ core-shell nanowire array on a film structure for the fabrication of ZnO-ZnGaON core-shell nanowire arrays. After the nitridation, the morphology of the dense nanowire array structure was maintained in the SEM observation. The energy dispersive spectrometer analysis examined on the surfaces of the core-shell nanowires revealed the existence of element nitrogen in the sample. The ultraviolet-visible diffuse reflectance analyses showed two absorption shoulders of the core-shell sample. The absorption in the UV region is likely attributed to the Ga and/or N doped ZnO cores and the absorption in the visible region is attributed to the ZnGaON material. A visible light sensitive photocurrent was obtained for the ZnO-ZnGaON core-shell nanowire sample when used as a photoanode in PEC water splitting cell with the on-off cycles of the visible light illumination (λ > 420 nm). The photocurrent of the fabricated ZnO-ZnGaON nanowire photoanode was ~ 20 times larger than the photocurrent obtained with the ZnO-$ZnGa_2O_4$ nanowire sample under visible light illumination (λ > 420 nm). Recently, an optimized nitridation was conducted on the ZnO-$ZnGa_2O_4$ core-shell nanowire sample, which largely increased the conductivity of the fabricated ZnO-ZnGaON sample as estimated from the two point measurement. A best delivered photocurrent density of ~ 1.7 mA/cm^2 was obtained with a nitridated ZnO-$ZnGa_2O_4$ nanowire photoanode under one sun light illumination (AM 1.5G solar simulator). The obtained large photocurrent of one nitridated ZnO-$ZnGa_2O_4$ nanowire photoanode is likely due to the appropriate nitridation treatment by which the ZnO-ZnGaON nanowire array was formed with a good conductivity. I expect the ZnO-ZnGaON nanowire photoanode fabricated with the optimized nitridation process will contribute efficiently to solar PEC water splitting.