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Effect of oxidation time on ZnO nanostructures prepared from Zn films by electro-oxidation

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Transparent semiconducting oxides, such as copper oxide, tin-doped indium oxide, fluorine-doped tin oxide, and zinc oxide (ZnO) have attracted considerable scientific attention owing to their unique properties. They are used in a wide variety of applications, including solar cells, surface-acoustic wave devices, and optoelectronic devices. ZnO which has a wide band gap (3.37 eV) and a high exciton binding energy (60 meV) is one of the promising materials for applications in optoelectronic devices operating in the ultraviolet (UV) region. Although various optoelectronic devices based on ZnO have been developed, it is important to grow ZnO films with high crystallinity to obtain good electrical and photoresponse properties. Structural defects in ZnO form defect-related states, which deteriorate the electrical properties, and surface defects deteriorate the photoresponse properties because of band bending. Therefore, it is essential to develop a method for preparing ZnO films with high crystallinity.

Various fabrication techniques, such as molecular beam epitaxy, chemical vapor deposition, thermal evaporation, and oxidation have been used to prepare highly crystalline ZnO film. Among these, the oxidation method is advantageous as it is simple and inexpensive. Thermal oxidation is the most well-known oxidation method, wherein a high quality ZnO film is obtained from metallic Zn films by applying heat at a temperature of 900 ℃ or above. Another oxidation method is the hot-water treatment method in which Zn is oxidized in hot water (90 ℃) for a long time to form high quality ZnO nanostructures. The former method requires a considerably high temperature, and cracks may occur when the difference in the thermal expansion coefficient between the substrate and the Zn film is large. In the latter, the process is carried out at a relatively low temperature, but requires a long time.

The electrochemical oxidation method can overcome the disadvantages of thermal and hot-water oxidation methods. In the electrochemical oxidation method, the formation of Zn(OH)2, which is a key product of oxidation by electrolysis of OH- from water, is accelerated, and Zn is rapidly oxidized to ZnO at a relatively low temperature. This method can be used to grow ZnO in the form of films or nanostructures depending on the oxidation temperature, thickness of the Zn film, oxidation time, current density, and pH of the solution. However, the mechanism of the oxidation process in this method has not been studied so far.

In the present work, we prepared ZnO nanostructures at various oxidation times by electrochemical oxidation and studied the growth mechanism of ZnO nanostructures based on the oxidation time. ZnO nanostructures were grown by oxidizing Zn films using the electrochemical oxidation method. According to the SEM images, the oxidation process for the formation of ZnO nanostructures consisted of three steps. First, Zn with a hexagonal columnar crystal was preferentially oxidized at the side surfaces because of the presence of relatively unstable planes, and then, Zn2+ which was ionized from the Zn (002) plane was crystallized on the ZnO crystal wall by combining with OH-. Finally, the formed ZnO crystals aggregated to form a tooth-like structure. This oxidation process was confirmed by the XRD results, which indicated a decrease in the intensity of the Zn (100) peak and a shift in the position of the Zn (002) peak to that of the ZnO (101) peak. As the oxidation time was increased, rearrangement of the crystals took place and the structural and surface defects were reduced, which decreased the non-radiative transition and increased the NBE emission. The photo responsivity and the photosensitivity of the ZnO nanostructures that were not sufficiently oxidized, i.e., at 1, 5, 10, and 20 min, were very low. However, the photoresponse properties of the ZnO nanostructures sufficiently oxidized at 30, 60, and 120 min gradually increased with increase in the oxidation time owing to rearrangement of the ZnO crystals. The enhanced photoresponse properties of the ZnO nanostructures are

promising for applications in optoelectronic devices.

Author: JEON, Wooseong (Injе University)

Co-author: Dr LEEM, Jae-Young (Department of Nanoscience & Engineering, Inje University)

Presenter: JEON, Wooseong (Inje University)

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