

XPS Study of ZnO Thin Films Annealing in Atomic Oxygen

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Zinc oxide materials have potential applications in optoelectronic devices. In order to create light-emitting devices on the base of ZnO it is necessary to obtain material of both *n*- and *p*- type. However, at present obtaining *p*-type material is a complex technological problem. It is connected with the fact that ZnO films and single crystals have *n*-type conductivity due to the large number of donor intrinsic defects, such as interstitial zinc or oxygen vacancies.

Typical *n*-type ZnO thin films were prepared using radio frequency magnetron sputtering. Thermally oxidized Si (111) wafers used as substrates. The thickness of the amorphous silicon oxide layer was 500 nm. Sputtering was performed using argon with 99.999% purity. A ZnO disc with 99.999% purity was used as a target. The thickness of the ZnO films about 500 nm. ZnO films were annealing in atomic oxygen at temperatures from 600°C. Atomic oxygen was generated using a 40 W rf discharge at a pressure of 0.1 Pa. The XPS spectra were used to confirm the stoichiometry of ZnO film.

XPS spectra, Zn 2p, Zn LMM and O 1s of the as-deposited and annealed ZnO films were studied. The Zn 2p_{3/2} peak of zinc in the elemental as well as oxide forms usually consists of a single component at the binding energy of 1021.8 eV. However, an asymmetric Zn 2p_{3/2} peak with components at binding energies of 1022.5 and 1021.6 eV is sometimes observed. The former is associated with Zn in the oxide form while the latter is attributed to metallic zinc.

Since the Zn 2p_{3/2} peak shape does not always give an asymmetric feature, the Zn LMM Auger peak analysis is often used to identify the chemical states of the zinc species. The deconvolution of the Zn LMM Auger peak reveals two components at kinetic energies of 991.7 and 988.5 eV, attributed to the presence of elemental Zn in the film and the bonding of Zn with oxygen in ZnO respectively.

We could observe that O1s peak position of the as-deposited ZnO film was at 531.2 eV, which indicated the film was in the oxygen deficient state. However O1s peak position of the annealed ZnO film was at 531.5 eV. We could find that oxygen binding energy shifted towards the large energy direction, which was attributed to increase in the oxygen atoms of the annealed ZnO film. Part of the increased oxygen atoms exist as Zn–O bond, and the rest as free oxygen.

From the results of XPS, we could obtain that the atom ratio of Zn:O equaled, respectively, 1:0.96 before being annealed and 1:1.06 after being annealed which showed that ZnO changed from Zn-rich to O-rich after being annealed in atomic oxygen.