XPS

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 12 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions.

Figure 1. Schematic representation of the XPS process

Physics

A typical XPS spectrum is a plot of the number of electrons detected (sometimes per unit time) (Y-axis, ordinate) versus the binding energy of the electrons detected (X-axis, abscissa). Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exists in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the area (volume) irradiated. To generate atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" (RSF) and normalized over all of the elements detected.

Sample preparation

Epitaxial zinc oxide films were grown on the GaN/Al2O3 substrate by Atomic Layer Deposition. They used diethylzinc as a zinc precursor and deionized water as an oxygen precursor. The ALD process was performed in reactor at 280 °C and ZnO layer thickness was about 2.0 µm.

Procedure

The morphology of the surface and structural quality of ZnO films obtained under these growth conditions are described elsewhere. In order to achieve As doping ZnO films were annealed in a sealed closed ampoule (SCA) under 2 atm arsenic ambient pressure at temperatures 850 °C, 910 °C and 950 °C for 1 h. Ampoule was first evacuated to the pressure of 10⁻⁴ atm, and arsenic pressure was obtained by inserting the appropriate amount of pure As. The content and electronic properties were derived from X-ray photoemission spectroscopy (XPS).

Data
Figure 2. The high-resolution XPS spectra of the As3d for ZnO-ALD films annealed in arsenic at temperature 950 °C (a) and 850 °C (b) and the As 3d component at BE = 44.3 eV, described to the AsZn-2VZn complex, dominates in the (a) spectrum. It is accompanied by the appearance of the ABE photoluminescence peak. Binding energy scale refers to the Fermi level and is adjusted to the C1s XPS peak position at the BE equal to 284.8 eV.
Analysis

In order to elucidate the chemical nature of As the ZnO films, we analyzed the high-resolution XPS spectra of the As3d peak. The As3d XPS spectra can be deconvoluted into the three As3d components, representing by As3d5/2-As3d3/2 doublets, situated at the binding energy (BE) of 41-41.5 eV, 44.3-45 eV and 47.4-48 eV, respectively (Figure 2). The component observed at the highest BE (47.4-48 eV) can be attributed to the As forming the As-O, i.e. arsenic atoms substituting oxygen (AsO). This kind of defect acts as a deep acceptor. In fact, we cannot exclude some contribution of elemental As in this BE region (42 eV), which was proved to be an amphoteric dopant in ZnO. According to the As3d contribution situated between BE 44.3 eV and 45 eV has been attributed to As-related complexes introducing AsZn and two zinc vacancies VZn. The creation of this kind of AsZn-2VZn defects has been proposed in order to explain p-type conductivity in As-doped ZnO.

In Figure 3, we show the Zn3d and the valence band XPS spectra taken after annealing at different temperatures. The low BE shift is observed in the Zn3d and the valence band spectra. The BE shift of about 0.5 eV is observed when the annealing temperature of ZnO:As films increases from 850? to 950?. This chemical shift can be evidently assigned to As dopant interaction with the ZnO lattice leading to formation of acceptors states in the ZnO:As film annealed at 950?.

References

1) http://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy
2) http://webh01.ua.ac.be/mitac4/micro_xpsaes.pdf