Effective Nitrogen Doping of Zinc Oxide

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Zinc oxide, like other transparent oxides, is an important material for next-generation short-wavelength opto-electronic devices. To realize these device applications, an important issue that needs to be addressed is how to fabricate both high quality p-type and n-type ZnO films. However, like most wide band-gap semiconductors, ZnO has an "asymmetric doping" limitation[1], i.e., it can be an easily doped high-quality n-type, but it is rather difficult to dope p-type. Nitrogen (a good p-type dopant for other II-VI semiconductors) has long been considered as a possible dopant for p-type ZnO, but various efforts have failed to realize this goal. The difficulty of making p-type ZnO has been attributed to low energy native point defects such as oxygen vacancies (V_O) and zinc interstitials (Zn_i), or to unintentional, but ever-present hydrogen.

It has long been known that under equilibrium conditions, the concentration of a point defect is mainly related to its formation energy, which depends on the chemical potentials of the host and relevant impurity atoms. In the case of ZnO, the native defects (vacancies, interstitials, and antisite defects) and various configurations and complexes that are possible for N need to be factored into consideration. For all practical purposes, the only relevant defects are substitutional N at an O site (N_O~which is an acceptor), substitional N_2 at an O site ($(N2)_O$-which is a donor), an oxygen vacancy (V_O~which is a donor), and a zinc interstitial (Zn_i~which is a donor). In broad perspective, it is the relative concentrations of these defects that control the doping type. According to recent theoretical studies, the formation energy of the desirable N_O defects is proportional to the chemical potential of oxygen[2]. In our case, this theory implies that more N_O defects can be obtained with decreasing oxygen partial pressure in the sputtering gas. In this work, we have studied the effect of oxygen partial pressure during sputtering process on nitrogen doping efficiency of zinc oxide and opto-electronic properties of ZnO:N films. Particular emphasis is being placed on understanding the relationship between the physical, chemical and electronic properties of the films and the observed photoelectrochemical performance. The results from XPS and Raman spectroscopic studies on the N-doped zinc oxides will be presented.

The nitrogen doped ZnO films used in this study were concurrently deposited on plain glass substrates for structural and electrical analyses and ITO-coated glass substrates for electrochemical characterization. The ZnO:N films were prepared by reactive RF sputtering of a zinc metal target with different oxygen partial pressures. The oxygen partial pressure in the sputtering gas was varied systematically from 0.5 to 3.0 mTorr and the total pressure ($N_2 + O_2$) during sputtering was maintained at 15 mTorr. ZnO:N film thicknesses were approximately 500 nm. Mott-Schottky experiments (in 1 M KCl) were performed using a potentio/galvanostat (Solartron 1286) and a Solartron model 1260/1265 frequency esponse analyzer. Pt foil and Ag/AgCl electrodes were used as the counter and reference electrode, respectively. Electrical properties of the films were characterized using Hall analyses (BioRad model HL5500 apparatus). X-ray diffraction (XRD) measurements were performed on a Scintag X-1 diffractometer using a Cu K□ radiation.

References

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