Recent Progress in Techniques for Producing Impurity-doped ZnO Thin Films Suitable for Transparent Electrode Applications

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As a result of the widely held belief that a stable supply of ITO may be difficult to sustain for the recently expanding market for optoelectronic devices because of the scarcity and high price of indium, impurity-doped ZnO materials such as Al- or Ga-doped ZnO (AZO or GZO) thin films have attracted much attention as promising substitutes [1,2]. We believe that current problems associated with substituting these doped ZnO for ITO can be resolved. In this paper, we describe recent progress in doped ZnO film deposition techniques to overcome two remaining problems, stable operation in various environments and low-resistivity film depositions on large area substrates with a high deposition rate. Impurity-doped ZnO thin films were prepared by a newly developed vacuum arc plasma evaporation (VAPE) method [3] as well as a high-rate dc magnetron sputtering (dc+rfMSP) deposition [4] that incorporates rf power with or without an introduction of H_2 gas into the deposition chamber. Because VAPE is a vacuum evaporation method that substitutes a high density Ar plasma for the electron beam used in EB evaporation, doped ZnO thin films can be deposited in a low energy plasma environment. We prepared transparent conducting GZO, FZO, BZO, and Ga and F-co-doped ZnO, and thin films with a low resistivity on the order of 10^{-4} Ωcm and a deposition rate above about 150 nm/min. The dc+rfMSP depositions were carried out by adding an rf component in the power range of 0-150 W to a constant dc power of 80 W. It is well known that in preparing doped ZnO thin films with standard magnetron sputtering methods, the resistivity of deposited films at substrate locations that correspond to the target erosion area pattern is always higher than that at the substrate location that corresponds to the target center. Using dc+rfMSP, however, the resistivity at substrate locations that correspond to the target erosion area decreased markedly as the rf power was increased up to about 60 W. This result demonstrates that a considerable improvement of resistivity distribution could be obtained by adding rf power. In addition, dc+rfMSP depositions that introduced H_2 gas produced thin films with relatively uniform resistivity distribution; the resistivity distribution considerably improved as the H_2 gas content was increased up to approximately 0.4%, reaching a relatively uniform distribution at a H_2 gas content of 0.4-0.6%. In addition, long-term stability tests of AZO and GZO films were carried out in various environments such as air at a relative humidity of 90% and a temperature of 60^{o}C. The resistivity of all AZO and GZO thin films was found to increase with exposure time when tested long term in a high humidity environment. However, dc+rfMSP depositions at a temperature of 200^{o}C could produce sufficiently moisture-resistant AZO thin films with a low resistivity below $5X10^{-4}$ Ωcm.

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[2] T.Minami: Semicond. Sci. Technol. 20 (2005) S35.
[3] T.Minami, S.Ida and T.Miyata: Thin Solid Films 445 (2003) 263.
[4] T.Minami, T.Miyata, Y.Ohtani and Y.Mochizuki: Jpn. J. Appl. Phys., 45 (2006) L409.