Synthesis and Characterization of Ag- or Sb-Doped ZnO Nanorods by a Facile Hydrothermal Route

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ZnO nanorods doped with Ag and Sb have been synthesized by a facile hydrothermal technique. Crystal quality, morphology, chemical/electronic composition, local structure, and vibrational mode properties are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and micro-Raman spectroscopy. Evidence of dopant incorporation is demonstrated in the XPS measurements of both Sb-doped and Ag-doped ZnO nanorods. From XRD data, it was found that the doped ZnO nanorods have a lower degree of crystallinity. The lattice constants of doped ZnO nanorods were slightly larger than that of the pure samples.

1. Introduction

Recently, zinc oxide (ZnO) nanorods have been extensively investigated due to their potential for the development of novel nanodevices. Their excellent properties such as a wide band gap (3.37 eV at 300 K), a large exciton binding energy (60 meV), and a large melting point of 1975 °C ensure applications in miniaturized photodetectors,[1,2] light emitting diodes,[3,4] laser light source,[5] and nanosensors[6,7] in harsh environments. For ZnO, addition of impurities often induces dramatic changes in their electrical and optical properties, which suggests new applications.

Usually, undoped ZnO exhibits *n*-type conductivity, which can be ascribed to the asymmetric doping limitations[8] and propensity to defects or impurities.[9,10] *P*-type doping of ZnO films has been achieved using P,[11] N,[12] As,[13] Li,[14] Sb,[15−18] and Ag[19,20] as dopants. These dopants and defect complexes, introduced through synthesis techniques, can define the type of conductivity[21] and optical[22,23] and electrical properties[22,24] of ZnO. A model for a large-sized mismatched group V dopant such as Sb in ZnO was reported in which a $Sb_{Zn}-2V_{Zn}$ complex was thought to be a suitable acceptor instead of a deep Sb_O acceptor.[15,16] Pure Ag- or Sb-doped ZnO has been effectively prepared by pulsed laser deposition,[16,19,26] radio frequency magnetron sputtering,[25,27] and molecular beam epitaxy.[28] Most of the above techniques employ physical means to dope impurities into ZnO, which do not ensure stoichiometric composition. The solution growth method, on the other hand, is a facile, low temperature, and low cost method that can produce high quality and stoichiometric ZnO material.

In this paper, we report an inexpensive, *template-free*, and rapid hydrothermal growth technique to dope ZnO nanorods at low temperatures. We compare the effectiveness of three different characterization techniques on the determination of the impurity incorporation into ZnO nanorods. We found that the effects of Sb and Ag dopants on the structural, chemical, and optical properties and vibrational modes of ZnO nanorods varied. While in X-ray photoelectron spectroscopy (XPS), the signals came directly from the impurities, so it is relatively straightforward to detect the impurity concentration. For X-ray diffraction (XRD) and Raman measurements, the signals came indirectly from the structural and vibrational mode changes due to the impurity incorporation, and therefore it is much more difficult to obtain impurity concentration information using these two methods.

2. Experimental Details

2.1. Synthesis. Slices of *p*-type Si(100) cleaved from a Si wafer were used as substrates for the synthesis of the ZnO nanorods. Before the synthesis process starts, the silicon (Si) substrates were sequentially cleaned with an acetone:ethanol (50:50) mixture in an ultrasonic bath and etched by piranha solution (2:1 mixture of concentrated H_2SO_4/30% H_2O_2) at room temperature for 25 min. Solvent (acetone or isopropylalcohol) was used to remove organic contaminants as reported before.[29,30] After this step, substrates were rinsed with deionized water and then blown dry with a flux of air[29,30] immediately before the hydrothermal process was started.

All the chemical reagents used in our experiments were of analytical grade and used without further purification. In a typical procedure, zinc sulfate heptahydrate [$Zn(SO_4)\cdot 7H_2O$] was first dissolved into 100 mL of deionized (DI) water, and

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