Epitaxial Growth and Polarity Control of Doped ZnO Heterostructures

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Abstract:

Zinc oxide (ZnO) is a transparent semiconductor with a band gap of 3.3 eV, having applications ranging from solar cells to transparent electrodes. It grows in a hexagonal wurtzite crystal structure with two different orientations, terminating in either an O- or a Zn-layer. These polarities have differing structural, optical, and electrical properties, although the ZnO polarization process is spontaneous and not well understood. For ZnO to be a more commercially applicable material, the polarization mechanism in electronic device applications must be controlled. For this research project, the attempts for controlling the orientation include annealing, introducing various thicknesses of a 1% mol. aluminum doped ZnO buffer layer, and doping the deposited ZnO with cobalt. The ZnO was deposited via pulsed laser deposition (PLD) rather than the commonly used technique of sputtering. PLD provides a more controlled alternative to sputtering, offering a high stoichiometric retention from deposition source to thin film, as well as good adhesion and minimal contamination. The structural and electronic properties of various epitaxial ZnO heterostructures were subsequently characterized to explore the effects of doping and buffer layers on the material properties. The results of this project seek to guide future research on the eventual realization of dilute magnetic semiconductors with the polarity control of ZnO.

Summary of Research:

Pure ZnO and pure Al-doped ZnO (AZO) were deposited via pulsed laser deposition on a yttria-stabilized zirconia (YSZ) substrate. After deposition, each sample was cut in half, and one part underwent annealing in an oxygen furnace for 4 hours at 1200 C. The x-ray diffraction (XRD) scans showed that both samples exhibit c-axis orientations due to peaks only at intervals around 34 degrees, as seen in Figure 2. The effects of annealing on surface morphology were shown from the atomic force microscopy (AFM) scans, where the as-grown sample has a rougher and randomly oriented surface.

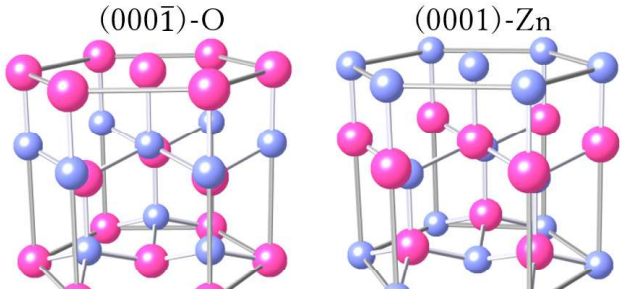

Figure 1: Diagram of oxygen polar and zinc polar ZnO crystals, respectively

This contrasts with the annealed sample, which was atomically smooth with some terraced steps that have heights corresponding to half the unit cell size of hexagonal ZnO. The Al dopant was added to increase carrier concentration, and this was tested by the temperature dependent Hall experiments ranging from 4 K to 300 K. This experimentation measured the as-grown AZO sample having a carrier concentration on the order of $10^{20}/cm^3$, while all other samples were of $10^{17}/cm^3$. Thus, aluminum proves to be an effective dopant in this system.

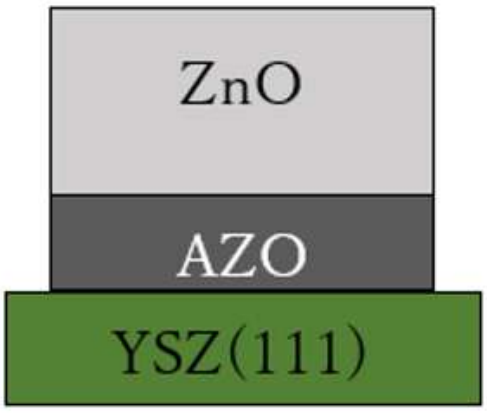

Figure 2: Layout of AZO-ZnO heterostructure deposited on a YSZ substrate

A previously established method of polarity determination using x-ray photoelectron spectroscopy (XPS) compares the intensity of two oxygen subpeaks around 5 eV, and a ratio greater than ~1.3 is a result typically characteristic of Zn-polar crystals. Using this method, it was determined that only the as-grown AZO crystal was Zn-polar while the annealed AZO, as-grown ZnO, and annealed ZnO were all O-polar.

Next, epitaxial heterostructures were fabricated with an AZO buffer layer of 5, 10, 30, 50, 100, and 200 nm thickness between the YSZ substrate and deposited ZnO, demonstrated in Figure 3. XPS analysis showed that as-grown samples with an AZO buffer layer thickness 30 nm and above were Zn-polar. Meanwhile, the 5 and 10 nm as-grown and all annealed samples, regardless of buffer layer thickness, were O-polar, shown in Figure 4. The annealed samples are likely all O-polar due to the annealing raising the thermal energy, promoting greater aluminum diffusion and creating an aluminum oxide surface layer. Having understood the effects of doping ZnO with Al and using AZO as a buffer layer, the final task was to apply this trend to Co-doped ZnO deposited on ZnO and AZO buffer layers. The cobalt doping did not change the film polarity, as the as-grown $Zn_{0.95}Co_{0.05}O$ was Zn-polar and the rest were O-polar. These results have demonstrated successful control over ZnO polarity control and can help contribute to the realization of better semiconductor devices in the future.

Conclusions and Future Steps:

Polarization control of ZnO crystals was achieved by introducing buffer layers of AZO with an appropriate thickness. These results were able to be applied to a ZnCoO system without affecting the orientation, which can lead to further development of semiconductor devices. Later work will focus on taking atomic resolution images via transmission electron microscope (TEM) on the film surfaces to better understand the interfacial structures. Once the sample has been fully measured, the materials will begin to be implemented into devices, and their properties will be characterized to ensure they are a viable component for the technology of the future.

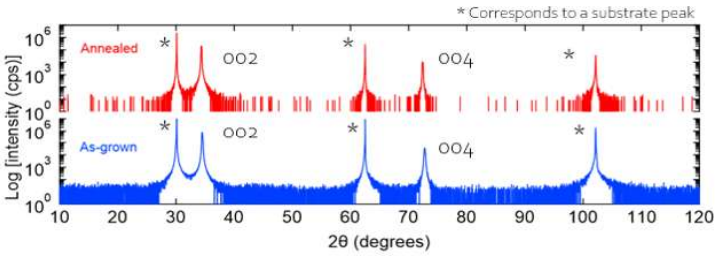

Figure 3: X-ray diffraction scan of annealed (top) and as-grown (bottom) ZnO

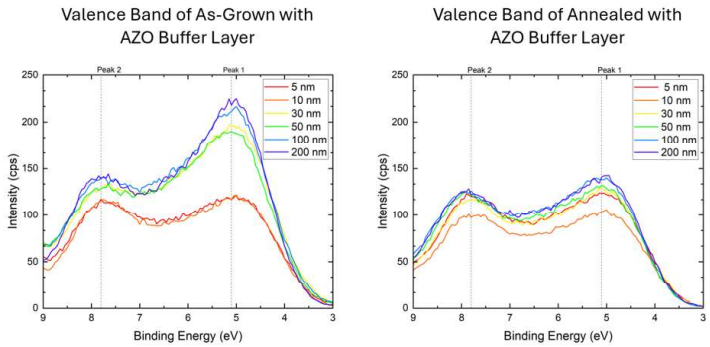

Figure 4: X-ray photoelectron spectroscopy scan of as-grown (left) and annealed (right) ZnO with varying AZO buffer layer thickness

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