XPS Analysis of Sulfide and Aluminum Nitride Based Buffer Layers for Epitaxial Zinc Oxide Growth

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Abstract:

Thin films of non-polar MnS and AlN/MnS were grown on Si <100> by PLD. The chemical compositions of the samples were investigated by angle-resolved XPS. It was found that AlN serves as a barrier to preserve MnS films from oxidation. It was also found that Mn-Si bonds existed on the surface of Si, while Si-S bonding was not observed. Finally, a native SiO_x layer was observed to diffuse to the surface of the sample, residing on top of epitaxial AlN. It is also likely that a thin Al_2O_3 layer existed alongside SiO_x.

Introduction:

Group III-V nitrides have become vital in the advancement of short wavelength opto-electronic devices. Using these materials, devices like the blue-green light-emitting diode (LED) have seen rapid development in recent years. For these devices to function at their maximum potential, epitaxial gallium nitride (GaN) films are necessary. More specifically, epitaxial growth of GaN on silicon (Si) <100> is necessary for integration of these devices in widespread technology. Unfortunately, there has been some difficulty in growing polar GaN <0001> on Si <100> substrates. In addition, the polar nature of GaN <0001> reduces the quantum efficiency through spontaneous and piezoelectric polarizations. Electrostatic fields that arise from these effects located at the interfaces of the heterostructure lead to band bending and separation of electron-hole pairs, as shown in Figure 1.

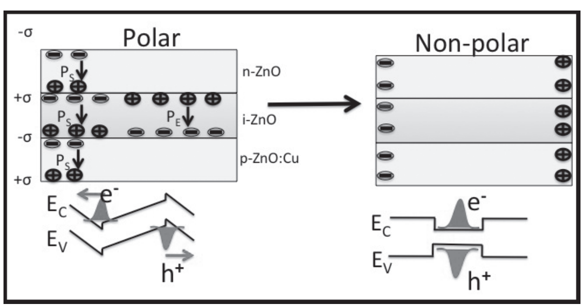

Figure 1: Electrostatic fields reduced in non-polar structure, resulting in reduction of bend bending and higher quantum efficiency [2].

In order to minimize these effects, work has been done to grow epitaxial non-polar <11-20> GaN on Si substrates. This goal was realized using manganese sulfide (MnS) <100> and aluminum nitride (AlN) <11-20> as buffer layers [1]. Work was done in this study to examine the chemical states that exist in these buffer layers.

Experimental Procedure:

Si <100> substrates were first cleaned by hydrogen fluoride (HF) etching to remove the native silicon dioxide (SiO_2) layer. MnS was deposited using pulsed laser deposition (PLD) using a substrate temperature of 700°C and pressure (P) of 3×10^{-7} torr to ensure clean MnS films. The film was then post-annealed for 30 minutes at 700°C and $P = 2 \times 10^{-7}$ torr to further improve the film quality. AlN was then deposited using PLD at a temperature of 700°C and $P(N_2) = 1 \times 10^{-4}$ torr, with a post anneal time of five minutes at 700°C. Analysis of the films was performed using angle-resolved x-ray photoelectron spectroscopy (XPS). Due to the shallow penetration depth of XPS, the thickness of MnS and AlN films were kept between 2.5-5.0 nm.

Results:

Figure 2 shows XPS results of the Sulfur 2p peak. Comparison of the left graph (2.5 nm MnS / Si) to the right graph (2.5 nm AlN / 2.5 nm MnS / Si) demonstrates that AlN acts as a protective layer for MnS against oxidation and allows for epitaxial MnS growth. Figure 3 shows XPS results of the Manganese 2p peak. The shoulder in the right graph is strongly indicative of Mn-Si bonding. In XPS larger angles correspond to information about deeper in the sample, so the sharp 90-degree peak and absence of a 30-degree peak means that Mn-Si bonding is located against the substrate.

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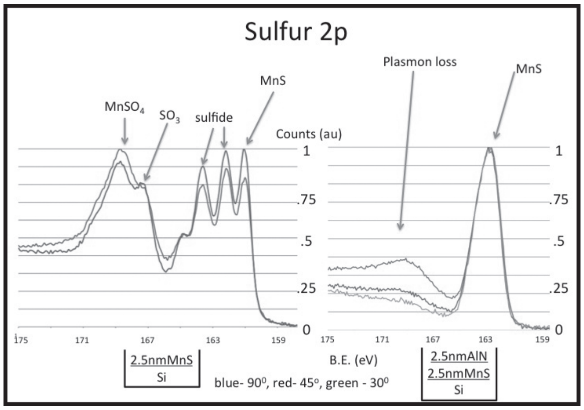

Figure 2: AlN acting as a protective layer for MnS, preventing other oxide states from forming.

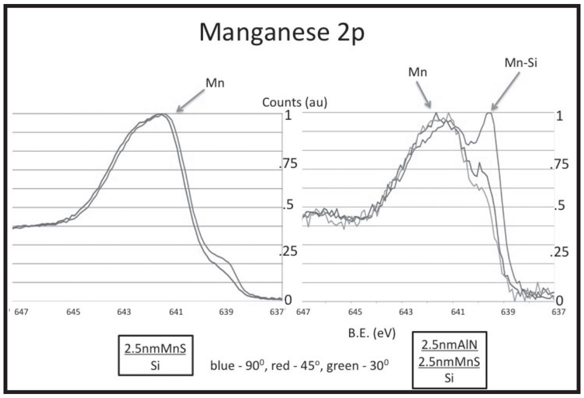

Figure 3: Formation of Mn-Si bonding observed in AlN/MnS/Si sample.

This result demonstrates that only Mn interacts with the Si substrate, while sulfur does not. While it is unclear whether there is a MnSi layer or if Si is simply bonding to Mn at the Mn/Si interface, Mn-Si bonding was clearly shown.

In addition, XPS analysis of the Silicon 2p peak (not shown) provided evidence that SiO_x is present in the structure. The angular resolution of the measurements showed that SiO_x diffuses to the surface of the thin-film structure, along with a probable monolayer of Al_2O_3. Examination of the aluminum and nitrogen peaks showed that AlN was epitaxial. These findings led us to model the buffer layer structure as shown in Figure 4.

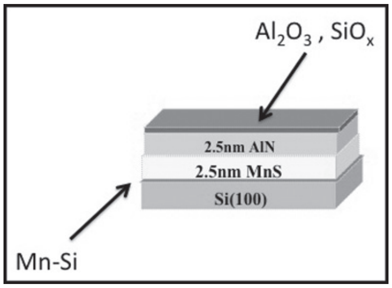

Figure 4: Model of buffer layer structure chemical composition.

Conclusions:

It was found that AlN serves as protective barrier for MnS against oxidation and that a thin layer of AlN allows for epitaxial MnS growth. From the Manganese 2p spectra, it was found that Mn-Si bonding is formed at Si/MnS interface while no S-Si bonding was formed. Lastly, SiO_x and Al_2O_3 (likely) exist at surface of structure. It was found that SiO_x diffuses to the surface of AlN regardless of the thickness of AlN.

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References:

[1] Song, J.-H., Y.-Z. Yoo, T. Sekiguchi, K. Nakajima, P. Ahmet, T. Chikyow, K. Okuno, M. Sumiya, and H. Koinuma. "Growth of Non-polar a-plane III-nitride Thin Films on Si(100) Using Non-polar Plane Buffer Layer." Physica Status Solidi (C) 2524 (7) (December): 2520-2524. doi:10.1002/pssc.200303444. http://doi.wiley.com/10.1002/pssc.200303444. 2003.

[2] Jeong-Hwan Song,"Epitaxial Growth of Nitride on Si with Sulfide Buffer Layer", Ph.D Dissertation, Department of Innovative and Engineered Materials, Tokyo Institute of Technology, 2002.