ABSTRACT

WANG, HAIYAN. Processing and Properties of Nitride-Based Thin Film Heterostructures. (Under the direction of Prof. Jagdish Narayan.)

The goals of this work were to synthesize nitride-based thin film heterostructures by Pulsed Laser Deposition, study the structural, mechanical, electrical and optical properties of these heterostructures and establish structure-property relations for these materials in order to further improve their properties and design new structures. Domain matching epitaxy was explored in most of these heterostructures and studied in detail for each case.

Mechanical and electrical properties of TiN as a function of microstructure varying from nanocrystalline to single crystal TiN films deposited on (100) silicon substrates were investigated. By varying the substrate temperature from 25°C to 700°C during PLD, the microstructure of TiN films changed from nanocrystalline to a single crystal epitaxial film. As the grain size decreased, the hardness of TiN films decreased (negative Hill-Petch relationship) and the resistivity of TiN increased.

High-quality epitaxial B1 NaCl-structured TaN films were deposited on Si(100) and Si(111) substrates with TiN as buffer layer, using pulsed laser deposition. Our method exploits the concept of lattice-matching epitaxy between TiN and TaN and domain-matching epitaxy between TiN and silicon. XRD, TEM, and STEM experiments confirmed the single-crystalline nature of the films with cube-on-cube epitaxy. The
stoichiometry of TaN films was determined to be nitrogen deficient (TaN$_{0.95\pm0.05}$) by RBS. Resistivity of the TaN films was found to be $\sim$220$\mu\Omega$-cm at room temperature with temperature coefficient of resistivity of -0.005K$^{-1}$.

Diffusivity of copper in single-crystal (NaCl-structured) and polycrystalline TaN thin films grown by PLD was investigated. The polycrystalline TaN films were grown directly on Si(100), while single-crystal films were grown with TiN buffer layers. The diffusion distances in epitaxial TaN are found to be about 5nm at 650$^\circ$C for 30 min annealing. The diffusivity of Cu into single crystal TaN follows the relation $D = (160 \pm 9.5) \exp\left[-(3.27 \pm 0.1)eV/k_BT\right]cm^2s^{-1}$ in the temperature range of 600$^\circ$C to 700$^\circ$C. Cu diffusion in polycrystalline TaN thin films is found to be nonuniform with enhanced diffusivities along the grain boundary.

By PLD, TiN and TaN targets were arranged in a special configuration that they can be ablated in a sequential manner to obtain uniform Ta$_x$Ti$_{1-x}$N alloy (x=30% & 70%) and TaN(3nm)/TiN(2nm) superlattice structure(x=60%). TiN buffer layers were deposited first to achieve those epitaxial binary components. XRD and TEM analysis showed the epitaxial nature of these films. Microstructure and uniformity of the superlattice and alloy structures were studied by TEM and STEM. Nanoindentation results suggested high hardness and future hard coating applications for these TiN-TaN composites. Four point probe electrical resistivity measurements and Cu diffusion characteristics study prove that TiN-TaN binary components provide a superior diffusion barrier for copper.
Uniform Al\(_x\)Ti\(_{1-x}\)N alloys (x up to 70%) and highly aligned TiN/AlN superlattices were deposited by PLD. Microstructure and uniformity for the superlattice structures and alloys were studied by TEM and STEM. Nanoindentation results suggested high hardness for these new structures and four point probe electrical resistivity measurements showed overall insulating behavior for both alloys and superlattices.

The epitaxial wurtzite AlN thin films were grown on (0001) \(\alpha\)-\(\text{Al}_2\text{O}_3\) substrates by PLD. XRD and SAD in TEM revealed the epitaxial growth of AlN on (0001) \(\alpha\)-\(\text{Al}_2\text{O}_3\) substrate. These AlN films were post-deposition annealed at 1300\(^\circ\)C for 30mins. Bright field and dark field TEM and transmittance spectra from the samples before and after annealing prove the annealing can effectively improve the quality of the film. Post-deposition annealing for AlN on \(\alpha\)-\(\text{Al}_2\text{O}_3\) substrates could be a very promising procedure for high quality optical device fabrications.

The epitaxial wurtzite AlN thin films were grown on (111) Si substrates by PLD and Laser-MBE. XRD and SAD in TEM revealed the epitaxial growth of AlN on Si(111) substrate. The interface structure and growth mechanism were studied by high-resolution TEM. Fourier filtered image of cross-sectional AlN/Si(111) samples from both Si <112> zone axes revealed the domain matching epitaxy of 4:5 ratio between \(a_{\text{Si}(110)}\) and \(a_{\text{AlN}(2\overline{1}T0)}\).
Processing and Properties of Nitride-Based Thin Film Heterostructures

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Prof. Carl C. Koch                     Prof. John Muth
This thesis is dedicated to my parents, my husband and my sister who give me wonderful support and encouragement all the way through my studies
Haiyan Wang was born on August 10th, 1976 in Hefei, China. She graduated from Hefei No.6 High School in 1994. In 1998 she graduated from the Dept. of Materials Science, Nanchang University in China. Her bachelor’s thesis work was focused on synthesis of Ultra-fine grains of ZnO and analysis of its properties. Due to her excellent academic record and research progress, she got the admission into master-degree-program without examination for the Institute of Metal Research, Chinese Academy of Sciences, in June 1998. She worked in Non-equilibrium and Fast-solidification National Laboratory headed by Dr. Lu and focused on magnetron sputtering deposition of nano-crystalline Cu thin film. She was accepted into the Ph.D. program by the Dept. of Materials Science and Engineering at North Carolina State University in Spring 2000. She worked under the direction of Prof. Jagdish Narayan for her Ph. D. Thesis.
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