SUMMARY

TiN: Using pulsed laser deposition, the grain size of TiN was varied from 8 nm to an epitaxial single crystal by changing the substrate temperature from 25^{o}C to 700^{o}C. The boundary angles are non CSL (coincidence site lattice) indicating the nonequilibrium nature of the dislocation arrangement. However, the grain boundary width remained the same at less than 1nm. The hardness of the TiN film was found to decrease with grain size of the crystal film. The decrease in hardness followed d^{n} behavior where n was found to be –0.4 and –1.2. This decrease in hardness with decreasing grain size is interpretted due to intergrain deformation or grain boundary sliding as proposed by Narayan and Conrad.[20,21] The resistivity results show the increasing resistivity as the grain size decreased. This can be reasoned as increasing grain boundary scattering. The combined mechanical and electrical properties of TiN films suggest the TiN as promising metallization materials and templates.

TaN: Single crystal NaCl-structured TaN films have been grown on silicon (100) and (111) substrate with TiN as a buffer layer using pulsed laser deposition. The transition from stable ε-TaN hexagonal phase (target) to metastable TaN cubic phase (films) was realized, leading to the formation of epitaxial films on Si(100) and Si(111) via TiN lattice matching. We have also conducted the studies on diffusion barrier characteristics of TaN for copper metallization and interconnections with very promising results.

Diffusion characteristics of Cu in TaN: The diffusion coefficient and diffusion activation energy of copper in single crystal NaCl-structured and polycrystalline TaN thin

films were investigated using TEM and STEM-Z contrast techniques. The diffusion coefficient D was determined to be $D = (160 \pm 9.5)\exp[-(3.27 \pm 0.1)eV / k_B T]cm^2 s^{-1}$ from 600°C to 700°C and the results were compared with polycrystalline TaN grown directly on Si (100). This study shows that epitaxial TaN with TiN buffer layer is a more effective diffusion barrier compared to polycrystalline TaN. Both single and polycrystalline TaN provide superior diffusion barrier characteristics for Cu than TiN thin films. A 5 nm thick single crystalline cubic TaN layer can effectively prevent Cu diffusion up to 650°C for 30min or less annealing time.

TaN/TiN superlattice and $Ta_XTi_{1-X}N$ alloys: We have investigated the binary components of TaN-TiN thin films as prospective diffusion barrier materials for Cu interconnects and high hardness coatings. By pulsed laser deposition and a special target configuration, TiN-TaN alloys and TiN/TaN superlattice structure were obtained by engineering the target configuration. 60% TaN resulted in superlattice of TaN(3nm) /TiN(2nm), while 30% and 70% TaN generated uniform $Ta_XTi_{1-X}N$ alloys. TiN buffer layers were deposited first to achieve those cubic epitaxial binary components and stabilize these metastable structures. Microstructure and uniformity of these superlattice and alloy structures were studied by TEM and Scanning transmission electron microscopy with Z-contrast (STEM). Nanoindentation results suggested high hardness for these new structures, especially superlattice structure has much higher hardness which suggest that TaN/TiN superlattice could be used as superhard coating. Resistivity measurements and Cu diffusion characteristics study indicate that both TaN/TiN

superlattice and TiN-TaN alloys provide a superior diffusion barrier for copper in next-generation integrated circuit devices.

AlN/TiN superlattice and $Al_XTi_{1-X}N$ alloys: Uniform cubic $Al_xTi_{1-x}N$ (x up to 70%) alloys and highly aligned TiN/AlN superlattice structures (x>80%) were synthesized on Si(100) using TiN buffer layer by pulsed laser deposition. Uniformity of these alloys and superlattice structures has been proved by transmission electron microscopy, scanning electron microscopy and scanning transmission electron microscopy (STEM, or Z-contrast). $Al_xTi_{1-x}N$ (x up to 70%) alloys are determined to be cubic structured nanocrystalline with slightly texture. For superlattice structure, it was observed that individual layers of AlN(4nm) and TiN(1nm) are highly textured cubic phases with no interface reaction. X-ray diffraction and TEM analysis proved the cubic $Al_xTi_{1-x}N$ (x up to 70%) alloys and cubic TiN/AlN nanoscale multilayers have been stabilized by thin layer of TiN buffer layer. Mechanical and electrical property studies suggest that $Al_xTi_{1-x}N$ (x up to 70%) alloys and AlN/TiN superlattices (x>80%) could be a promising candidate for coatings in high speed cutting tool and electronic packaging. Further studies on the stability of these metastable cubic $Al_xTi_{1-x}N$ (x up to 70%) alloys and TiN/AlN superlattice structure are needed for these future applications.

AlN/a-Al_2O_3: We have grown the epitaxial crystalline wurtzite AlN thin films on (0001) a-Al_2O_3 substrate by pulsed laser deposition. The epitaxial growth mechanism of this system was explored. The epitaxial relations of AlN on (0001)a-Al_2O_3 were observed to be (0001)AlN // (0003)a-Al_2O_3, $(01\bar{1}0)$AlN//$(2\bar{1}\bar{1}0)$a-Al_2O_3, and $(2\bar{1}\bar{1}0)$AlN //

$(01\bar{1}0)$a-Al_2O_3. High temperature annealing at 1300°C, which is within the temperature window, was performed to decrease the dislocation density. The TEM study and optical transmission measurements prove that quality of the AlN films increase dramatically with the dislocation reduction and defects annihilation. The mechanism of annealing effect is considered to be solid phase epitaxy of AlN from the interface layer.

AlN/ Si(111): We have grown the epitaxial crystalline wurtzite AlN thin films on (111) Si substrates by pulsed laser deposition and laser-molecular-beam-epitaxy. The epitaxial growth mechanism of this system was explored. The epitaxial relations of AlN on Si(111) are revealed as AlN[0002] // Si[111], AlN $[2\bar{1}\bar{1}0]$// Si[110], and AlN $[01\bar{1}0]$ // Si[211]. Atomic clean interface with steps, the transition layer from AlN ABCABC stacking sequence to ABAB stacking sequence and domain matching epitaxy of 4:5 ratio between the interplanar distance of Si (110) and AlN $(2\bar{1}\bar{1}0)$ were observed and reasoned as the possible mechanisms for epitaxial growth of AlN on Si(111) substrate. Due to MBE has higher vacuum capability, the interfaces grown by laser-MBE are sharper than normal PLD. An interface reaction layer was found in PLD grown AlN sample at temperature higher than 800°C. The deposition parameters which control atomic clean surface and films quality can be adjusted to further improve the quality of the epilayer, such as minimizing the stacking faults, domain boundary and dislocation density.