CHAPTER 4. EPITAXIAL GROWTH OF TaN THIN FILMS ON Si(100) AND Si(111) USING TiN BUFFER LAYER

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4.1 Abstract

We have deposited high-quality epitaxial B1 NaCl-structured TaN films on Si(100) and Si(111) substrates with TiN as buffer layer, using a pulsed laser deposition. Our method exploits the concept of lattice-matching epitaxy between TiN and TaN and domain-matching epitaxy between TiN and silicon. X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning transmission electron microscopy (Z-contrast) 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 Rutherford backscattering. Resistivity of the TaN films was found to be ~220μΩ-cm at room temperature with temperature coefficient of resistivity of $-0.005K^{-1}$.

4.2 Introduction

Recently, Cu has been widely used as interconnect material due to its low resistivity and high resistance to electromigration and stress migration.[1,2] However, Cu diffuses very easily into SiO_2 dielectric layers and subsequently into silicon region during device fabrication. Various diffusion barriers for Cu interconnection have been extensively studied.[3,4,5] Due to the higher thermal stability requirement and thickness limitation for next generation ULSI devices, TaN has become a very promising diffusion barrier material.[6] In previous studies, polycrystalline TaN films have been deposited by a variety of techniques: metal-organic chemical vapor deposition[7], radio-frequency and DC sputtering[8, 9], and ionized metal plasma[10]. Since TaN has different stable phases (such as solid-solution α-Ta(N), hcp-γ-phase, and hexagonal ε-phase) and metastable phases (such as bcc β-TaN, hexagonal δ-phase TaN, hexagonal WC structure θ-TaN and B1 NaCl-structured TaN),[11, 12] the structural and electrical properties of polycrystalline TaN films vary a lot with different deposition techniques. Furthermore, these polycrystalline films tend to grow columnar with grain boundaries normal to the substrate. These grain boundaries of TaN provide faster (pipe) diffusion paths for Cu and reduce its effectiveness as a diffusion barrier. This warrants the deposition of single crystalline TaN films. The single crystalline B1 NaCl-structured TaN film deposition has recently been reported on MgO(100) substrates.[13] However, for microelectronic applications it is desirable to grow single crystalline TaN on Si. In this letter, we report the integration of single crystalline TaN with Si(100) and Si(111) with a buffer layer of TiN, using a pulsed laser deposition.

4.3 Experimental

The depositions of TaN and TiN were performed in a multitarget chamber with a KrF excimer laser (Lambda Physik 210 λ= 248 nm, 10 Hz). The targets were hot-pressed stoichiometric TaN and TiN obtained from CERAC Inc. The TaN target was determined to be ε-TaN with hexagonal structure (a=0.5185, c=0.2908, c/a=0.561), while TiN target was NaCl type cubic. TaN and TiN films were deposited at a base pressure of about 1×10^{-7} Torr and substrate temperature 600 ± 10^{o}C. Crystal structure of these films was determined by X-ray diffraction using a Rigaku X-ray diffractometer with CuK_{α} radiation and Ni filter. Microstructural characterization of these films was performed by high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) using a JEOL-2010F analytical electron microscope with point to point resolution of 0.18 nm(TEM) and 0.12 nm(STEM). The epitaxial TaN films grown on MgO (100) under the same conditions were used for Rutherford backscattering (for stoichiometry), and four-probe resistivity measurements over the temperature range 12-300K.

4.4 Result and discussion

Figure 1(a) shows an X-ray diffraction pattern (intensity vs. 2θ) of an epitaxial TaN thin film on Si (100) using TiN as a buffer layer. The first two close peaks, centered at 41.66^{o} and 42.42^{o} are indexed as (200) TaN and (200) TiN, respectively. Second order (400) TaN and (400) TiN peaks are shown at 90.68^{o} and 93.18^{o}. All of these four peaks are

aligned with (400) silicon diffraction, suggesting that both TaN and TiN have grown epitaxially on Si(100).

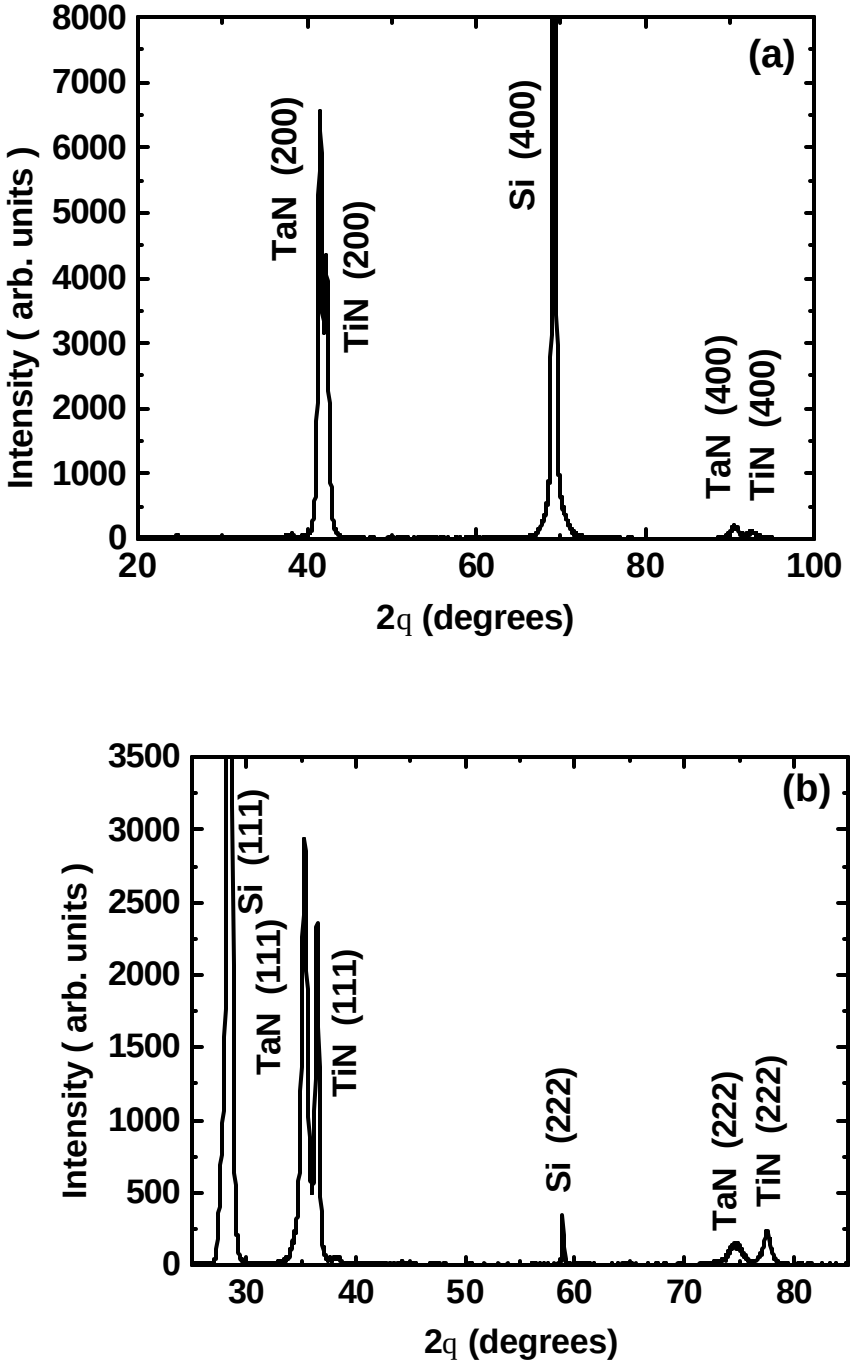

Fig. 1(a) XRD pattern (intensity vs. 2θ) showing (200) peaks from TiN and TaN film on Si (100) substrate; (b) XRD pattern showing (111) peaks from TiN and TaN film on Si (111) substrate.

The calculated d-space for TaN (200) and TiN (200) are 0.2165 nm and 0.2128 nm respectively and lattice mismatch of these two films is about 1.724%. The calculated lattice parameter for TaN is 0.4330 nm, which is slightly smaller than TaN on MgO (a=0.4335 nm)[13]. The X-ray diffraction pattern of TaN/TiN/Si(111) (see Fig.1(b)) shows that TaN (111) and TiN (111) are aligned with Si(111), suggesting the epitaxial growth of TaN on Si(111) is similar to that of TaN on Si(100).

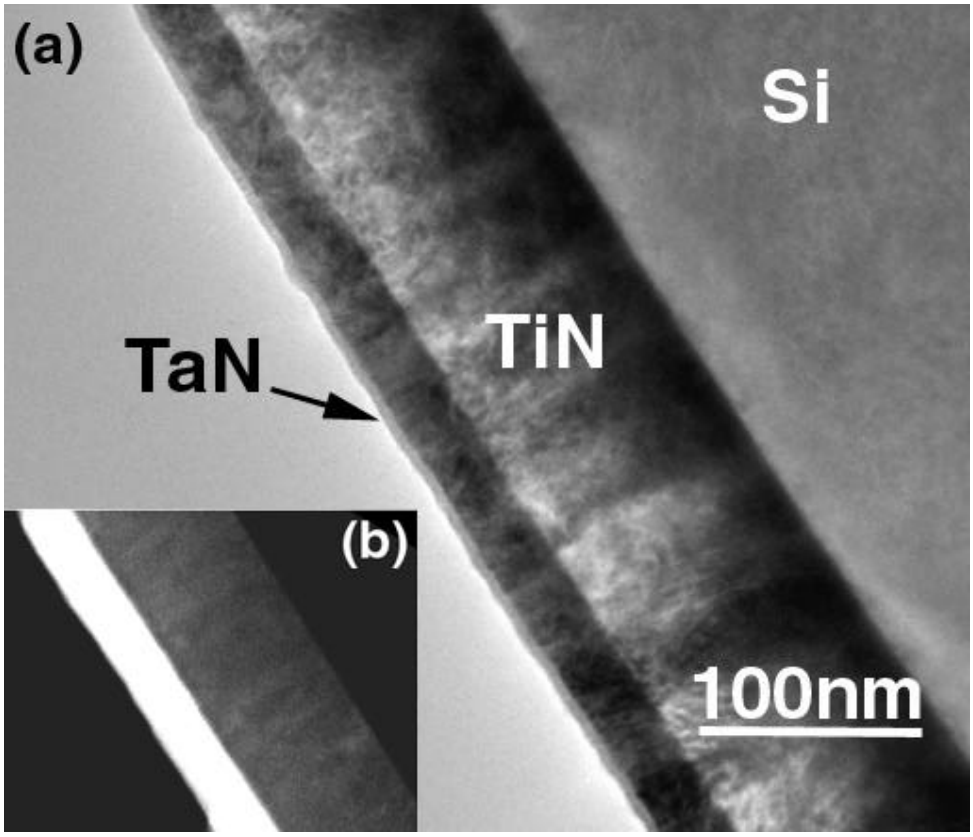

Fig. 2(a) Low magnification <110> cross-section image of epitaxial TaN/TiN/Si (100); (b) STEM-Z contrast image from <110> cross-section sample of TaN / TiN / Si(100)

The low magnification <110> cross-section TEM image of epitaxial TaN/TiN/Si (100) in figure 2(a) shows the film quality from large area of the film. The thicknesses of TaN and TiN layers on Si(100) were close to 25 nm and 100 nm respectively. A STEM-Z contrast image from <110> cross-section sample of TaN/TiN/Si(100) clarified the sharp interfaces of TaN/TiN and TiN/Si without any indication of interfacial reactions, as shown in figure 2(b). The TaN layer shows the brightest contrast compared to TiN and Si, because the STEM-Z contrast is proportional to Z^2 and the atomic number of Ta is 73, which is much larger than those of Ti (22) and Si (14).

The corresponding selected-area-diffraction pattern from <110> cross-section samples of TaN/TiN films on Si(100) shows epitaxial relation of TaN <110> // TiN <110> // Si<110> in figure 3(a). Figure 3(b) shows a diffraction from TaN indicating the high quality of the TaN film with calculated lattice parameter 0.4320 nm. The simulated diffraction pattern of TaN <110> // TiN <110> // Si <110> (see figure 3(c)) confirmed the single crystalline TaN and TiN films with cube-on-cube epitaxial relationship. Only high order diffractions from TaN and TiN can be distinguished due to a small difference in d-spacing. Since the cross-section specimens in both {100} and {111} silicon were prepared in <110> orientation, the diffraction patterns from TaN/TiN on Si(111) and TaN / TiN on Si(100) were identical.

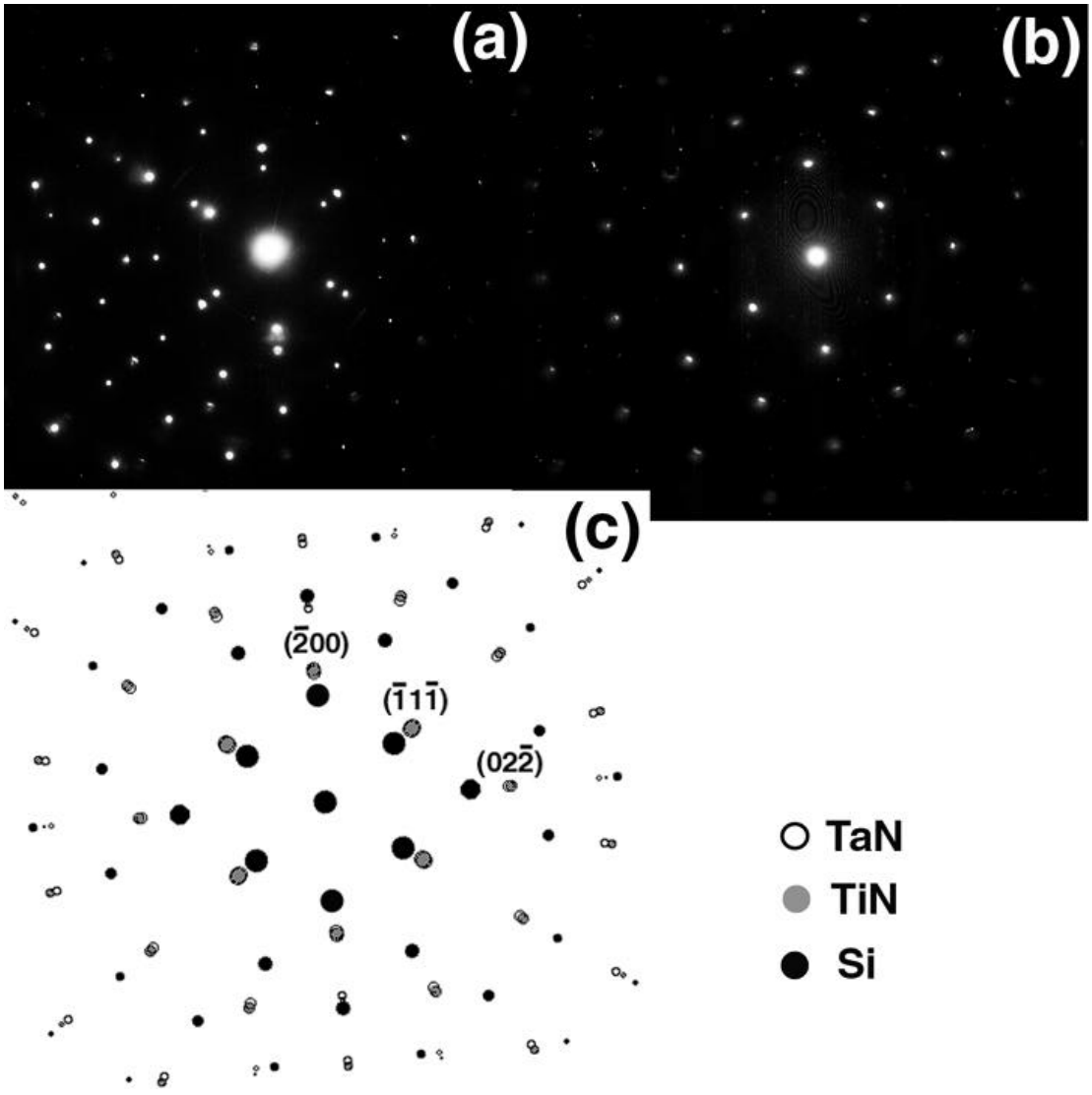

Fig. 3(a) Selected-area-diffraction pattern of TiN and TaN films on Si(100), cross-section of TaN <110> // TiN <110> // Si<110>; (b) Selected-area-diffraction from TaN film <110> only; (c) Simulated selected-area-diffraction pattern of TiN and TaN films on Si(100) along the <110> direction (TaN <110> // TiN <110> // Si<110>).

High Resolution <110> cross-section images of the epitaxial TaN/TiN interface and TiN/Si(100) interface are shown in Figure 4(a) and 4(b), respectively. Both of the interfaces are quite sharp without any indication of an interfacial layer. The {111} lattice planes of the two materials are well aligned. Small lattice mismatch and low interfacial energy result in no misfit dislocations along the TaN/TiN interface, because even after several hundred atomic layers of the coherent epilayer growth, the strain energy is not sufficient to overcome the activation energy for nucleation of dislocation at the free surface. On the other hand, the interface of TiN/Si contains a large lattice mismatch. In figure 4(b), misfit dislocations are clearly visible along the interface of TiN/Si and marked as the extra half planes of dislocation in figure 4(c). The short ordering of these misfit dislocations is clearly observed as 3:4 relationship, which means that 4 atomic planes of TiN (111) align with 3 atomic planes of Si(111), according to domain matching epitaxy.[14] The TaN phase directly deposited on Si(100) or Si(111) was found to be polycrystalline hexagonal ε-TaN, which is the stable phase of TaN, and the same as the target. The formation of metastable B1 NaCl-structured TaN is facilitated by the lattice matching substrate TiN and the nonequilibrium characteristics of PLD (the average energy of laser ablated species~1000kT). The reason that only TiN can be grown domain-epitaxially on silicon in the moderate vacuum range of 10^{-6} torr, is that in this case a few monolayers of native oxide can react with Ti, while in the case of TaN and MgO on Si(100), the native oxide disrupts the domain epitaxy. However, under an ultra high vacuum condition on atomically clean silicon, it should be possible to grow epitaxial TaN and MgO directly on silicon substrates.

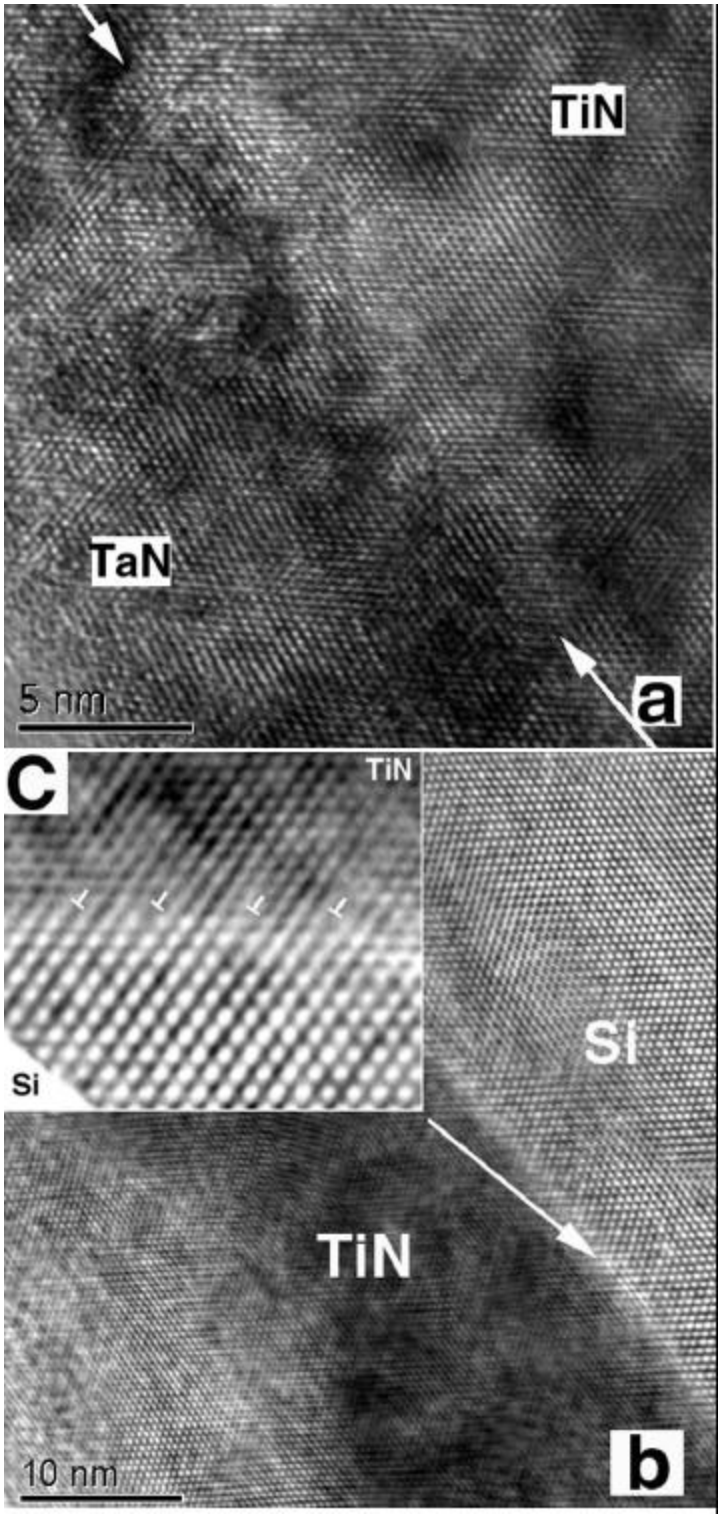

Fig. 4(a) High Resolution <110> cross-section image at interface of epitaxial TaN / TiN; (b) High Resolution <110> cross-section image of epitaxial TiN (Ts=700^{o}C) on Si(100);

and (c) Magnified part from interface between TiN and Si, the marked area is the extra half plane.

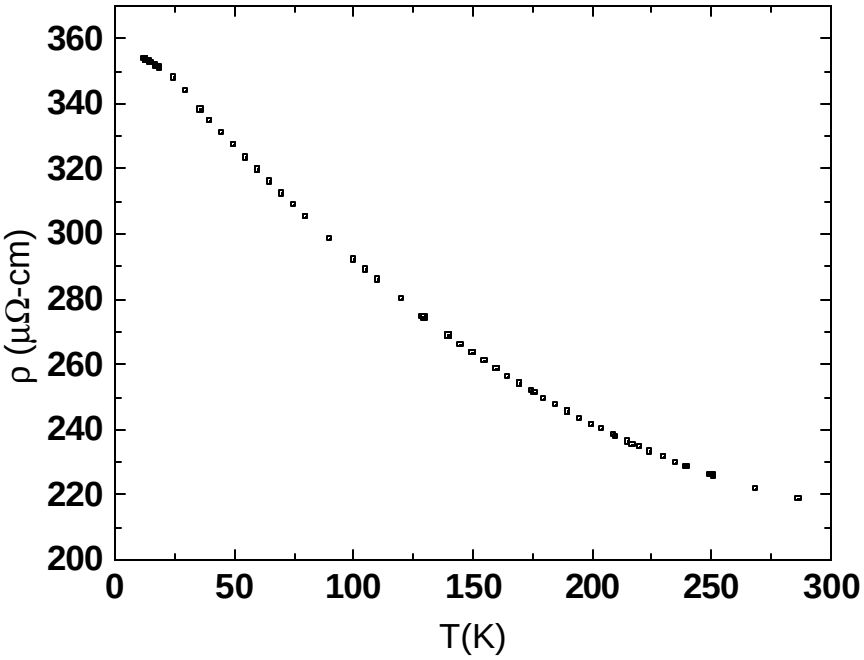

Fig.5 Resistivity of epitaxial TaN film on MgO vs. temperature (range from 12K to 300K).

The epitaxial TaN films grown on MgO (100) under the same condition of growth as on silicon were used for Rutherford backscattering (for stoichiometry measurements) and electrical resistivity measurements. The N to Ta ratio was estimated to be 0.95 ± 0.05 (slightly nitrogen deficient), which is close to stoichiometry. The resistivity of these films over the temperature range 12-300K is shown in figure 5 with room temperature resistivity ~220μΩ-cm and a rather small temperature coefficient of resistivity of -0.005K^{-1}, which are close to the previous report.[13] However, we observed that, when TaN is grown on TiN, the overall resistivity of TaN/TiN layer is dominated by

the resistivity of TiN. In order to check the stability and diffusion barrier properties of TaN/TiN films on Si, we grew Cu on top of these films and annealed up to 650^{o}C for 30 min. No perceptible diffusion of Cu in TaN films was found according to TEM, STEM(Z-contrast) and EELS(Electron energy loss spectroscopy) analysis.

4.5 Conclusions

In conclusion, 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.

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