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Single Crystal TaN Thin Films on TiN/Si Heterostructure

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ABSTRACT

We have successfully grown epitaxial cubic (B1-NaCl structure) tantalum nitride films on Si (100) and (111) substrate using a pulsed laser deposition technique. A thin layer of titanium nitride was used as a buffer medium. We characterized these films using X-ray diffraction, high resolution transmission electron microscopy and scanning transmission electron microscopy (Z-contrast). X-ray diffraction and high-resolution transmission electron microscopy confirmed the single crystalline nature of these films with cubic-on-cubic epitaxy. The epitaxial relations follow TaN(100)//TiN(100)//Si(100) on Si(100) and TaN(111)//TiN(111)//Si(111) on Si(111). We observed sharp interfaces of TaN/TiN and TiN/Si without any indication of interfacial reaction. Rutherford backscattering experiments showed these films to be slightly nitrogen deficient ($TaN_{0.95}$). High precision electrical resistivity measurements showed excellent metallic nature of these films. We also tried to deposit TaN directly on silicon, the films were found to be polycrystalline. In our method, TiN plays a key role in facilitating the epitaxial growth of TaN. This method exploits the concept of lattice matching epitaxy between TaN and TiN and domain matching epitaxy between TiN and Si. We studied the diffusion barrier properties of these films by growing a thin layer of copper on the top and subsequently annealing the films at 500°C and 600°C in vacuum. Cu diffusion layer was about 2nm after 600°C annealing for 30min. This work explores a promising way to grow high quality TaN diffusion barrier on silicon for copper interconnection.

INTRODUCTION

Interests in structural and electrical properties of tantalum nitride thin films has been stimulated by its promising applications as diffusion barriers in ultra-large-scale integration (ULSI) of Si integrated circuit.[1] Recently, Cu has been widely used as interconnect material due to its low resistivity, high electromigration and stress migration resistance, that are superior to Al and Al alloy interconnects.[2] However, Cu is very easy to diffuse into SiO_2 dielectric and subsequently into silicon region during device fabrication, which is deleterious to device operation. Various diffusion barriers for Cu diffusion have been extensively studied.[3-5] But all of these diffusion barriers were around 100nm in thickness. For next generation ULSI devices, the thickness of barrier layers is expected to be within 10 nm, which should prevent Cu diffusion at temperatures above 600°C for 30mins. TaN barrier layers become promising candidates.[6]

In previous studies, polycrystalline TaN films have been deposited by a variety of techniques: Metal-organic chemical vapor deposition,[7] radio-frequency sputtering method [8], DC magnetron sputtering[9] and ionized metal plasma[10]. TaN has different stable phases such as solid-solution α-Ta(N), hcp-γ-phase, and hexagonal ε-phase and metastable phases include bcc β-TaN, hexagonal δ-phase TaN, hexagonal WC structure θ-TaN and B1 NaCl-structured TaN.[11,12] Those stable and metastable phases make the structural and electrical properties of polycrystalline TaN films vary greatly from different deposition techniques.[7-10] Further more, those polycrystalline films tend to grow columnar with grain boundaries normal to the substrate. Those grain boundaries of TaN provide the faster diffusion path for Cu and reduce the effectiveness as diffusion barrier. The single crystalline B1 NaCl-structured TaN grown on MgO(100) substrates is reported recently with stoichiometry of $TaN_{1.22}$ and negative temperature coefficient of resistivity.[13] In order to realize TaN integration with silicon, the growth of high quality single crystalline NaCl-structure TaN on Si(100) and Si(111) became the main focus of this study. We have chosen TiN as buffer layer (a=0.4240nm) to grow TaN (a=0.4330nm) on Silicon (100) and (111) substrate by pulsed laser deposition. These heterostructures were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution TEM, STEM (Z-contrast). We grew TaN films on MgO under same condition for RBS and Four–probe resistivity measurements. Diffusion barrier properties of these films were studied by growing a layer of Cu on top of these single crystal TaN on Si substrate and annealed at different temperatures in vacuum.

EXPERIMENTAL

Pulsed laser deposition of TaN and TiN was performed in a multitarget chamber with a KrF excimer laser (Lambda Physik 210 λ= 248 nm). The energy density and pulse frequency were 1.5-3 J/cm^2 and 10 Hz respectively. 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 cubic having NaCl type structure. TaN and TiN films were deposited at a base pressure of about 1×10^{-7} Torr with a turbomolecular pump, substrate temperature was 600±10°C. No background gas was used to deposit these films. The laser deposition at 10 Hz repetition rate resulted in approximately 100 nm thick TiN film in 10 min deposition and 25 nm thick TaN film in 20 min on both Si(100) and Si(111). Crystal structure of these films was determined by X-ray diffraction using a Rigaku X-ray diffractometer with CuK_α radiation and Ni filter. The epitaxial TaN films grown on MgO (100) under the same condition were used for Rutherford backscattering (for stoichiometry measurements) and four-probe resistivity measurements over the temperature range 12-300K. Cu layers were grown on top of single crystal TaN sample on Si substrate at room temperature and were annealed for 500°C and 600°C for 30min. Microstructural characterization of these as deposited and annealed films was performed by high resolution transmission electron microscopy (HRTEM) and Scanning transmission electron microscopy (STEM) using JEOL-2010F analytical electron microscope with point to point resolution of 0.18 nm.

RESULTS AND DISCUSSION

Figure 1(a). shows X-ray diffraction pattern of epitaxial TaN thin film on silicon (100) using TiN as the buffer layer deposited at 600°C . The two close peaks, centered at 41.66° and 42.42°, are indexed as (200)TaN and (200)TiN seperately. Second order (400)TaN and (400)TiN peaks are shown at 90.68° and 93.18°. All of these four peaks aligned with (400) silicon diffraction indicate that both TaN and TiN have grown textured along (100) of silicon. The calculated d-space for TaN(200) and TiN (200) are 0.2165 nm and 0.2128 nm accordingly. The resulted lattice parameter for TaN is 0.4330 nm, which is slightly smaller than TaN on MgO (a=0.4335 nm)[13]. The close peaks of TaN (200) and TiN (200) show good lattice match of these two films with the lattice misfit of about 1.724%. X-ray diffraction pattern of TaN /TiN/ Si(111) is shown in figure1(b). TaN (111) and TiN (111) are aligned with Si(111), which shows that the TaN epitaxial growth on Si(111) is identical with TaN on Si(100).

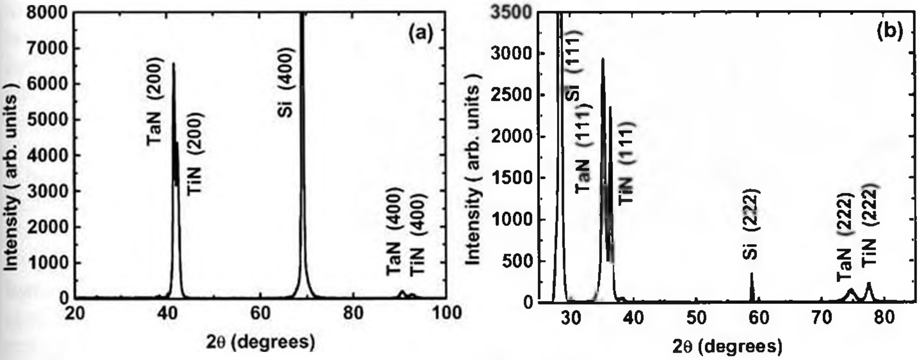


Fig. 1(a) XRD pattern (intensity vs. 2θ) showing (200) peaks from TiN and TaN film on Si (100) substrate; (b) XRD pattern showing (111) peaks from TiN and TaN film on Si (111) substrate.

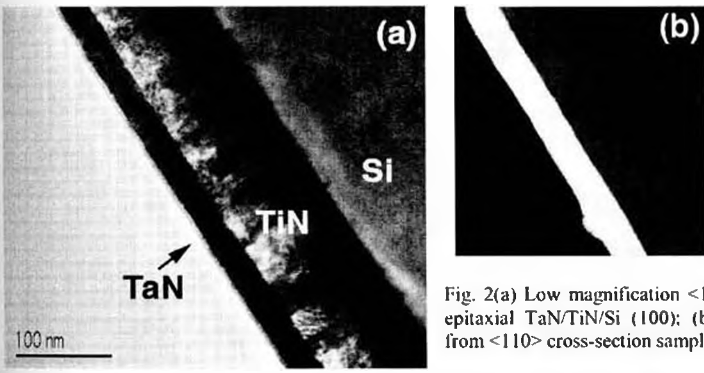


Fig. 2(a) Low magnification <110> cross-section image of epitaxial TaN/TiN/Si (100); (b) STEM-Z contrast image from <110> cross-section sample of TaN / TiN / Si(100)

Low magnification <110> cross-section transmission electron microscopy image of epitaxial TaN/TiN/Si (100) in figure 2(a). shows the film quality from large area of the film. The interfaces of TaN/TiN and TiN/Si are sharp without any indication of interfacial reactions. STEM-Z contrast image from <110> cross-section sample of TaN/TiN/Si(100) also clarified the sharp interfaces of TaN/TiN and TiN/Si in figure 2(b). The contrast is proportional to Z^2. Atomic number for Ta is 73, which is much larger than Ti and Si, so the TaN layer shows the brighter contrast than TiN and Si.

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). It is very difficult to distinguish TaN and TiN in the diffraction pattern because of small d-space difference. Figure 3(b) shows only the diffraction of TaN from the same area in order to observe the quality of TaN film. The calculated d-spacing of TaN(200) from the selected area diffraction pattern is about 0.2155 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 cubic-on-cubic epitaxial relationship. In the larger orders of diffraction pattern, the diffraction information from TaN and TiN is distinguishable. All the diffraction patterns for <110>cross-section samples of TaN / TiN on Si(111) are identical with the films on Si(100).

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>).

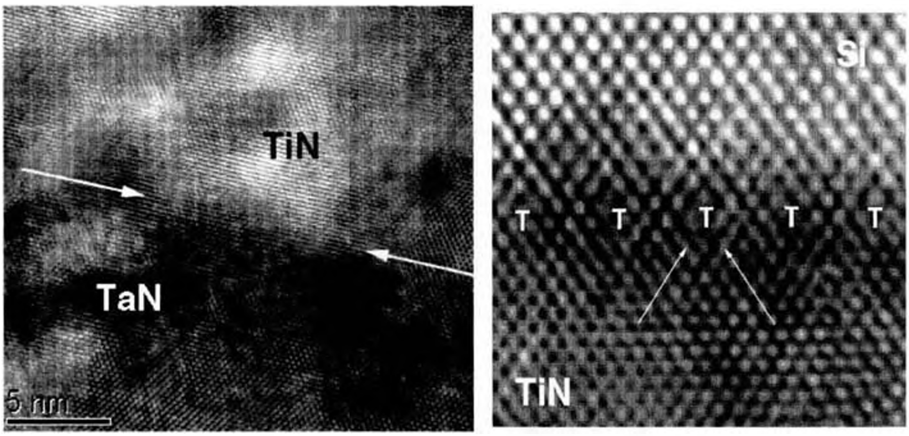
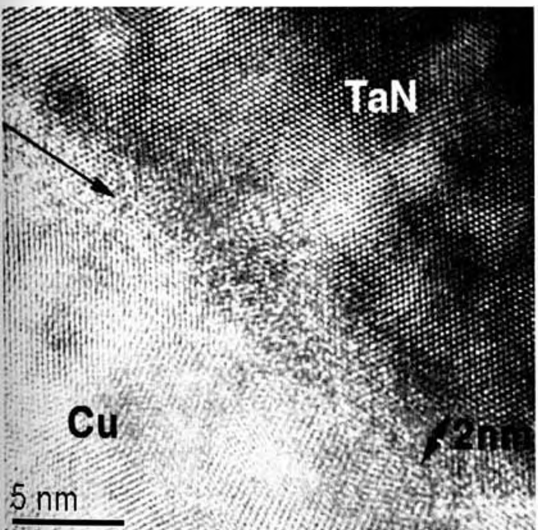


Fig. 4(a) High Resolution <110> cross-section image at interface of epitaxial TaN / TiN; (b) High Resolution <110> cross-section image of epitaxial TiN (Ts=600°C) on Si(100) with marked area is the extra half plane.

High Resolution cross-section images of epitaxial TaN/TiN (Ts=600°C) interface and TiN/Si(100) interface are shown in Figure 4(a) and 4(b) respectively. The interface of TaN and TiN is quite sharp without any indication of interfacial layer. The {111} lattice planes of both materials are well aligned. No misfit dislocations are present along the interface. In TaN/TiN small lattice mismatch systems with low interfacial energy, two-dimensional-growth is expected. Since the lattice mismatch of TaN and TiN is very small, 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. So no lattice mismatch dislocations could nucleate at the surface or move to the interface. Quite different from the TaN/TiN interface, the interface of TiN/Si belongs to large lattice mismatch case. In figure 4(b), the {111} lattice planes of these two materials are aligned and misfit dislocations are clearly visible along the interface of TiN/Si. The marked atomic planes indicate the extra half planes of dislocation generated along the interface. The short ordering of these misfit dislocations is clearly observed as 3:4 relationship, which means that 4 atomic planes of TiN (111) aligned with 3 atomic planes of Si(111).[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 such as TiN and MgO, which provide template for growth. The nonequilibrium characteristics of PLD also facilitate the formation of cubic phase because the average energy of laser ablated species is about three order of magnitude higher than the equilibrium value kT.

The epitaxial TaN films grown on MgO (100) under the same condition were used for Rutherford backscattering (for stoichiometry measurements) and electrical resistivity measurements. N to Ta ratio is about 0.95 ± 0.5 (nitrogen deficient), which is close to stoichiometry. The resistivity of these films over the temperature range 12-300K was measured by four point probe and room temperature resistivity is about 220μΩ-cm and temperature coefficient of resistivity is -0.5μΩ-K^{-1}. For the TaN grown on TiN buffer layer, the overall resistivity is mainly controlled by TiN and showing good metallic nature.



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 at 500°C and 600°C for 30mins. No diffusion of Cu in TaN films was found after 500°C annealing for 30min. For 600°C annealing, we found the diffusion layer of Cu is about 2 nm in HRTEM cross-section image of Cu/TaN/TiN/Si. Figure 5. shows the cross-section high-resolution TEM image of the Cu/TaN/TiN/Si sample annealed at 600°C for 30min with 2nm-thick Cu diffusion layer marked. The calculated Diffusion coefficient for Cu diffusion in single crystal TaN at 600°C is about $10^{-18} cm^2 s^{-1}$, according to Fick's first and second law. ($X=\sqrt{D\tau}$)

Fig. 5. High resolution TEM image of <110> cross-section sample of Cu on single crystal TaN / TiN / Si(100) after 600°C annealing for 30 min. The uniform diffusion layer is clearly marked to be about 2nm;

CONCLUSIONS

Single crystal tantalum nitride films have been grown on silicon (100) and (111) substrate with titanium nitride as buffer layer. X-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution TEM of these films indicate single crystal nature of the films with cubic-on-cubic epitaxy. High-resolution microscopy and Z-contrast (STEM) of cross-section samples revealed sharp interface of TaN/TiN and TiN/Si without any indication of interfacial reaction. Rutherford backscattering analysis indicates the stoichiometry of TaN films is nitrogen deficient ($TaN_{0.95\pm0.05}$). Resistivity of the TaN films was found to be ~220μΩ-cm at room temperature with temperature coefficient of resistivity of -0.5μΩK^{-1}. Cu diffusion layer in these single crystal TaN was about 2nm after 600°C annealing for 30min. This work explores a promising way to grow high quality NaCl-structured TaN diffusion barrier on Silicon for copper interconnection.

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