Mat. Res. Soc. Symp. Proc. Vol. 745 © 2003 Materials Research Society N6.11

Copper Diffusion Characteristics in Single Crystal and Polycrystalline TaN

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ABSTRACT

TaN has become a very promising diffusion barrier material for Cu interconnections, due to the high thermal stability requirement and thickness limitation for next generation ULSI devices. TaN has a variety of phases and Cu diffusion characteristics vary with different phases and microstructures. We have investigated the diffusivity of copper in single-crystal (NaCl-structured) and polycrystalline TaN thin films grown by pulsed laser deposition. The polycrystalline TaN films were grown directly on Si(100), while the single crystal films were grown with TiN buffer layers. Both of poly and single-crystal films with Cu overlayers were annealed at 500°C, 600°C, 650°C, and 700°C in vacuum to study the copper diffusion characteristics. The diffusion of copper into TaN was studied using STEM-Z contrast, where the contrast is proportional to Z^2 (atomic number), and TEM. The diffusion distances ($2\sqrt{D\tau}$) are found to be about 5nm at 650°C for 30 min annealing. The diffusivity of Cu into single crystal TaN follows the relation $D = (160 \pm 9.5)\exp[-(3.27 \pm 0.1)eV / k_B T] cm^2 s^{-1}$ in the temperature range of 600°C to 700°C. We observe that Cu diffusion in polycrystalline TaN thin films is nonuniform with enhanced diffusivities along the grain boundary.

INTRODUCTION

Interests in structural and electrical properties of tantalum nitride thin films have been stimulated by their 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] These 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. Based on these complexities, we have recently reported the epitaxial growth of NaCl-structured TaN on Si(100) and Si(111) with a buffer layer of TiN, using a pulsed laser deposition[13], where we explored the lattice-matching epitaxy of TaN and TiN and domain matching epitaxy of TiN and Si.[14] So far no report on the diffusivity of copper in single crystal cubic NaCl-structured TaN is found in the literature. In order to determine the diffusion characteristics of the single crystalline cubic TaN, we grew a layer of Cu on top of the TaN samples at room temperature and annealed at different temperatures. The diffusivity of Cu into these single crystal cubic TaN films and diffusion activation energy are evaluated and compared with the results of polycrystalline TaN films directly grown on Si by pulsed laser deposition.

EXPERIMENTAL

Depositions of Cu, TaN and TiN layers were performed in a multitarget chamber with a KrF excimer laser (Lambda Physik 210 λ= 248 nm, 10 Hz). Single crystal cubic TaN was grown on Si(100) with TiN buffer layer, the details of which are discussed elsewhere.[13] Polycrystalline TaN was grown directly on Si(100) with the same substrate temperature (600±10°C) as for the single crystal TaN. The Copper film was deposited on single and poly crystalline TaN films at room temperature with the backpressure of 1×10^{-8} torr. Crystal structures of these as-deposited films were determined by X-ray diffraction using a Rigaku X-ray diffractometer with CuK_α radiation and Ni filter. The Cu-deposited specimens were annealed at 500°C, 600°C, 650°C, and 700°C in vacuum of about 3×10^{-6} Pa. Detailed microstructural and Cu-diffusion studies were 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 STEM-Z contrast technique, where contrast varies as Z^2 (atomic number), was used to determine Cu diffusion characteristics.

RESULTS AND DISCUSSION

Low magnification <110> cross-section transmission electron microscopy image of epitaxial TaN/TiN/Si (100) in figure 1(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 1(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 2(a). It is very difficult to distinguish TaN and TiN in the diffraction pattern because of small d-space difference. Figure 2(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 2(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).

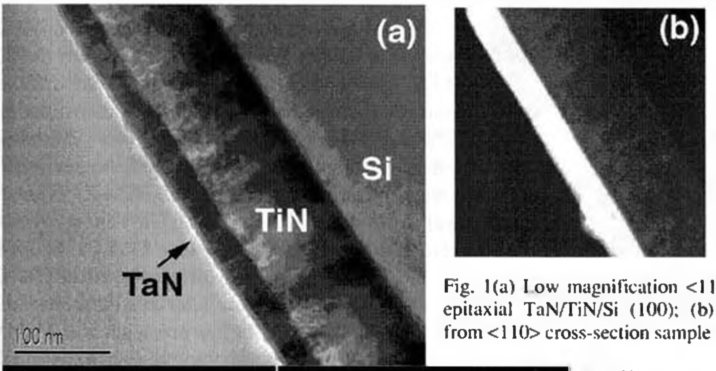

Fig. 1(a) Low magnification <110> cross-section image of epitaxial TaN/TiN/Si (100); (b) STEM-Z contrast image from <110> cross-section sample of TaN / TiN / Si(100)

Fig. 2(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>).

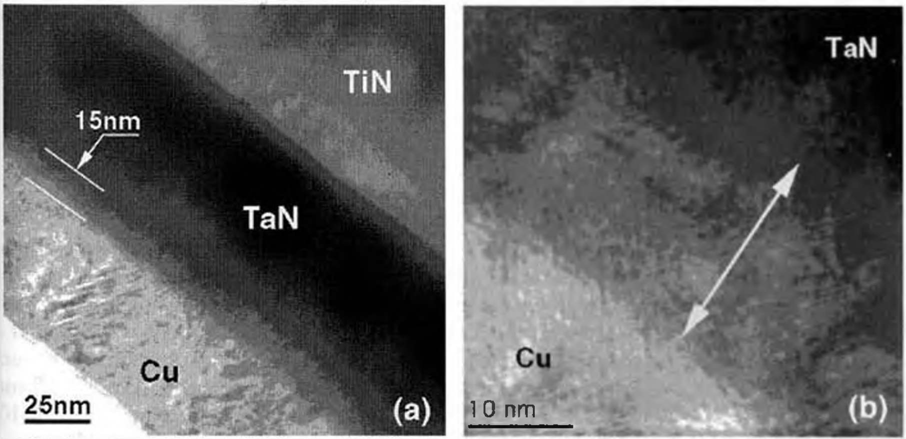

Fig.3. (a) Low magnification TEM image of <110> cross-section sample of Cu on single crystal TaN / TiN / Si(100) after 700°C annealing for 30 min. The uniform diffusion layer is clearly marked with depth of about 15nm; (b) High resolution TEM image of interface of TaN and Cu with marked diffusion layer.

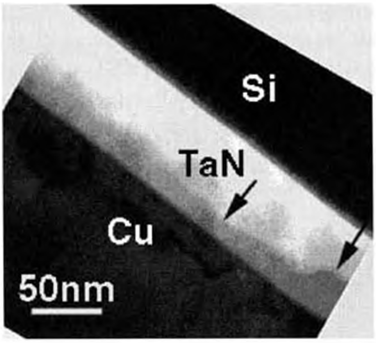

Fig.4. STEM-Z contrast image from <110> cross-section sample of Cu on polycrystalline TaN / Si(100) after 700°C annealing for 30 min, showing a nonuniform diffusion layer.

In the case of Cu diffusion studies in single crystal TaN, we annealed Cu/TaN/TiN/Si samples at 500°C, 600°C, 650°C, and 700°C in vacuum. The diffusion distances (penetration depths) were determined using TEM and STEM-Z contrast techniques. Based upon the contrast differences, the diffusion distances were averaged from many TEM and STEM-Z contrast images taken from different area along Cu/TaN interface. The average diffusion distances were found to be 2nm, 5nm, and 15nm after annealing at 600°C, 650°C, and 700°C / 30min, respectively. After 500°C annealing, no perceptible diffusion into TaN was detected and the interface between Cu and TaN remained sharp. The results for 700°C sample are shown in a <110> cross-section TEM image of Cu/TaN/TiN/Si (100) in figure 3(a). Grain growth of Cu layer is obvious and no oxidation of Cu is observed in the annealed samples. High resolution TEM image (figure 3b) of the interface between TaN and Cu from the same area clearly shows the atomic structure of the diffusion layer. The Cu diffusion layer is uniform along the interface of TaN and Cu. The STEM-Z contrast image also indicates the uniformity of the diffusion layer and proves Cu diffuses into single crystalline TaN via bulk diffusion mechanism only. In contrast to the single crystal TaN diffusion barrier, the polycrystalline TaN diffusion barrier layer gave varying Cu penetration depth as shown in STEM-Z contrast image from <110> cross-section polycrystalline TaN/Si(100) after 700°C annealing for 30min.(Figure 4) The TaN layer shows up with brighter contrast compared to Si and Cu, because the STEM-Z contrast is proportional to Z^2 and the atomic number of Ta is 73, which is larger than Si (14) and Cu (29). Inside the TaN film, a layer with slightly darker contrast indicates the Cu diffusion layer. The thickness of the Cu diffusion layer varies from 15 nm to 27 nm. The nonuniformity is due to the grain boundaries in polycrystalline TaN which provide faster diffusion path, because the activation energy for the grain boundary diffusion is approximately half of the bulk diffusion value.[15]

Based on Fick's first and second law and infinite-source-diffusion approximation, the average diffusion length of atoms can be expressed by equation:

$$C(x,\tau) = C_s erfc(\frac{x}{2\sqrt{D\tau}}) \qquad \text{-----------(1)}$$

where, C_s is the surface concentration, 'erfc' is the complementary error function, x is the penetration (diffusion) depth, D is the diffusion coefficient at certain temperature, and τ is the time for diffusion. When the argument of the complimentary error function becomes unity, the concentration of copper becomes about 16% of its surface value. A rough estimation of diffusion coefficient can be made by equating the argument of complimentary error function to unity and using the different observed penetration depths at different temperatures (Einstein Formula[16]). The D value for 700°C, 650°C, and 600°C were calculated to be in the range of 10^{-16} –10^{-18} cm^2/s (see Figure 5). According to Arrhenius relation, D should follow the relation:

$$D = D_0 \exp(-Q_0 / k_B T) \qquad \text{----------(2)}$$

where Q_0 is the activation energy of atomic diffusion, D_0 is the pre-exponential factor and k_B is the Boltzmann constant. The diffusivity evaluated from figure 5 is

$D = (160 \pm 9.5)\exp[-(3.27 \pm 0.1)eV / k_B T]cm^2 s^{-1}$. ----------(3)

Because in the single crystalline TaN, Cu diffusion is mainly controlled by bulk diffusion mechanism, 3.27eV can be considered as the activation energy for bulk diffusion. If the existing of low angle grain boundaries and other defects in the films is considered, the activation energy would be even higher than 3.27eV as the film quality improved. Based upon the assumption that grain boundaries consist of systematic arrays of dislocations, the activation energy for the grain boundary diffusion is about half of the lattice (bulk) diffusion.[15] Therefore, Q_0 for grain boundary diffusion is estimated to be approximately 1.6eV, which is about 6 times larger than the activation energy for Cu diffusion into TiN (Q_0 = 0.29eV) by grain boundary mechanism reported by Lim et al.[17] This shows that TaN can be a better diffusion barrier material for Cu interconnections. Our values of activation energy compare reasonably well with literature values of 1.3 eV for grain boundary diffusion from 600 to 800°C and 2.7 eV for bulk diffusion from 800 to 900°C.[6] These films were deposited by RF sputtering technique and the microstructure/ defect content, (which play an important role in diffusion), were not reported.[6] Possible reasons for the better diffusion barrier characteristics of our single crystal NaCl-strucutured TaN are considered to be lack of short diffusion paths, due to grain boundaries, and therefore, the lattice diffusion dominates. For a net transport along the grain boundaries, we need to include the boundary width (~0.5nm) to explain differences in the Cu diffusion layers between single crystal and polycrystalline regions. Also, since pulsed laser deposition is a non-equilibrium process, ratios of Ta / N in ablated single crystal TaN films are determined to be 0.95 ± 0.05 (determined by RBS channeling)[13], which is close to the stoichiometric composition. The absence of excess nitrogen vacancies in our samples provides more reliable values of activation energies. Furthermore, cubic NaCl-structured TaN is a low resistivity phase compared to other TaN phases. Thus the single crystalline NaCl-structured TaN using TiN buffer layer can provide a superior diffusion barrier for Cu interconnections in next-generation IC devices.

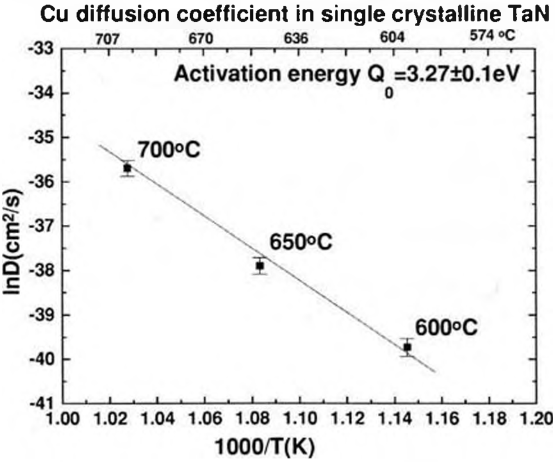

Fig.5. Arrhenius plot showing the diffusion coefficients of Cu in single crystalline cubic TaN barrier layer with temperature varing from 550 to 700°C.

CONCLUSIONS

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.

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