

## Copper diffusion characteristics in single-crystal and polycrystalline TaN

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We have investigated the diffusivity of copper in single-crystal (NaCl-structured) and polycrystalline TaN thin films grown by pulsed-laser deposition. Polycrystalline TaN films were grown directly on Si(100), while single-crystal films were grown with TiN buffer layers. Both poly- and single-crystal films with Cu overlayers were annealed at 500, 600, 650, and 700 °C in vacuum to study the copper diffusion characteristics. The diffusion of copper into TaN was studied using scanning transmission electron microscopy (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 5 nm 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<sup>2</sup> s<sup>-1</sup> in the temperature range of 600–700 °C. We observe that Cu diffusion in polycrystalline TaN thin films is nonuniform with enhanced diffusivities along the grain boundary. © 2002 American Institute of Physics. [DOI: 10.1063/1.1502193]

TaN has become a very promising diffusion barrier material for Cu interconnection because of the high thermal stability requirement and thickness limitation for next-generation ultra-large-scale integrated (ULSI) devices.<sup>1–3</sup> Since TaN has a variety of stable phases [such as solid-solution  $\alpha$ -Ta(N), hcp- $\gamma$  phase, and hexagonal  $\varepsilon$  phase] and metastable phases (such as bcc  $\beta$ -TaN, hexagonal  $\delta$ -phase TaN, hexagonal WC structure  $\theta$ -TaN and B1 NaCl-structured TaN),<sup>4,5</sup> not only the structural and electrical properties, but also the diffusion characteristics of polycrystalline TaN films vary considerably with deposition techniques<sup>6,7</sup> and nitrogen concentration.<sup>8–10</sup> Besides, grain boundaries provide a fast diffusion path for Cu that requires taking into account the Cu diffusion along the grain boundaries, which may vary with the grain size of the polycrystalline diffusion barrier.<sup>11</sup> 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 pulsed-laser deposition,<sup>12</sup> where we explored the lattice-matching epitaxy of TaN and TiN and domain-matching epitaxy of TiN and Si.<sup>13</sup> 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 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.

Depositions of Cu, TaN, and TiN layers were performed in a multitarget chamber with a KrF excimer laser (Lambda Physik 210  $\lambda = 248$  nm, 10 Hz). Single-crystal cubic TaN was grown on Si(100) with a TiN buffer layer, the details of which are discussed elsewhere.<sup>12</sup> On the other hand, polycrystalline TaN was grown directly on Si(100) with the same substrate temperature ( $600 \pm 10$  °C) as for single-crystal

TaN. A copper film was deposited on single and poly-TaN films at room temperature with the backpressure of  $1 \times 10^{-8}$  Torr. Crystal structures of these as-deposited films were determined by x-ray diffraction (XRD) using a Rigaku x-ray diffractometer with Cu  $K\alpha$  radiation and a Ni filter. Cu-deposited specimens were annealed at 500, 600, 650, and 700 °C in vacuum of about  $3 \times 10^{-6}$  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 the Cu diffusion.

Figure 1 shows an x-ray diffraction pattern (intensity versus  $2\theta$ ) of Cu grown on epitaxial TaN on a TiN/Si(100) heterostructure before annealing. The first two close peaks, centered at 41.66° and 42.42° are indexed as (200) TaN and (200) TiN, respectively. Both of these peaks are aligned with (400) silicon diffraction, which shows that TaN and TiN have grown on the Si(100) substrate with the same surface normal

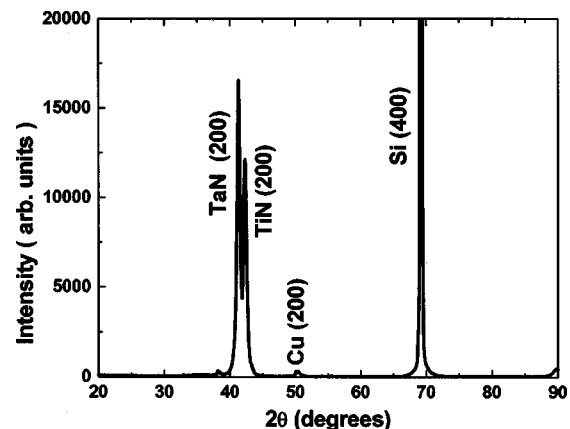


FIG. 1. XRD pattern (intensity vs  $2\theta$ ) showing (200) peaks from TiN, TaN, and room-temperature deposited Cu film on a Si(100) substrate.

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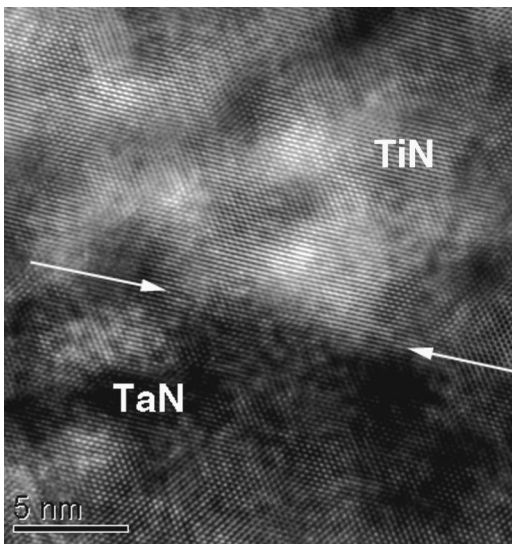


FIG. 2. High-resolution  $\langle 110 \rangle$  cross-section image showing the interface of epitaxial TaN/TiN.

$\langle h00 \rangle$ . The third peak corresponds to (200) Cu, showing the preferred orientation for copper as well. A high-resolution  $\langle 110 \rangle$  cross-section image of the TaN/TiN interface is shown in Fig. 2, which clearly shows alignment along all three axes or epitaxial growth of TaN on single-crystal TiN. The  $\{111\}$  lattice planes of the two materials are well aligned. A small lattice mismatch and low interfacial energy result in almost no misfit dislocations along the TaN/TiN interface. For TaN films directly grown on Si(100) without a TiN buffer layer, the samples were determined to be polycrystalline  $\epsilon$ -TaN, because the polycrystalline hexagonal  $\epsilon$ -TaN is more stable than the metastable B1 NaCl-structured TaN. The present results clearly show that the cubic NaCl structure of TaN is stabilized by the similar structure of TiN.

In the case of Cu diffusion studies in single-crystal TaN, we annealed Cu/TaN/TiN/Si samples at 500, 600, 650, 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 areas along the Cu/TaN interface. The average diffusion distances were found to be 2, 5, and 15 nm after annealing at 600, 650, and 700 °C/30 min, respectively. After 500 °C annealing, no perceptible diffusion into TaN was detected and the interface between Cu and TaN remained sharp. The results for the 700 °C sample are shown in a  $\langle 110 \rangle$  cross-section TEM image of Cu/TaN/TiN/Si (100) in Fig. 3(a). Grain growth of the Cu layer is obvious and no oxidation of Cu is observed in the annealed samples. The high-resolution TEM image [Fig. 3(b)] 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 the bulk diffusion mechanism only. In contrast to the single-crystal TaN diffusion barrier, the polycrystalline TaN diffusion barrier layer gave varying Cu penetration depths, as shown in the STEM-Z contrast image

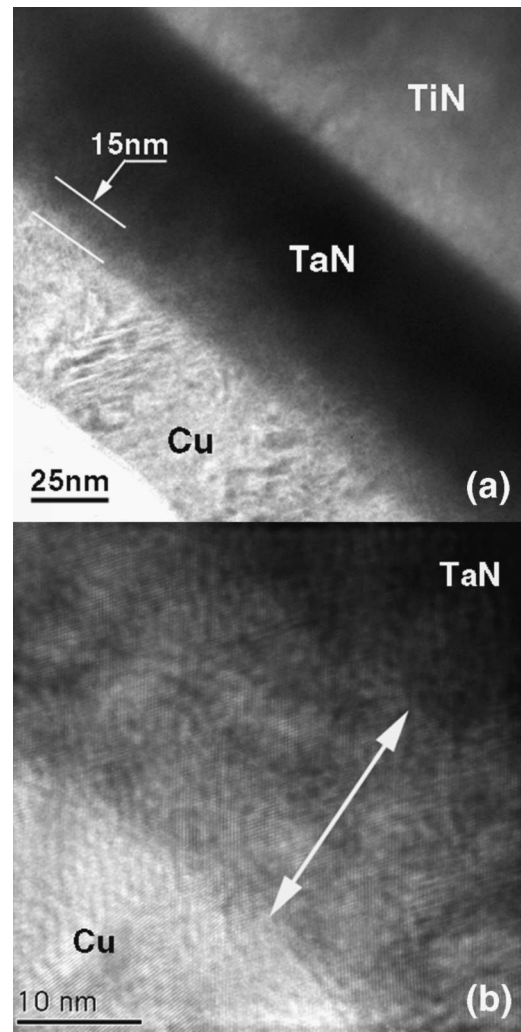


FIG. 3. (a) Low-magnification TEM image of the  $\langle 110 \rangle$  cross-section sample of Cu on single-crystal TaN/TiN/Si(100) after 700 °C annealing for 30 min. The uniform diffusion layer is clearly marked with a depth of about 15 nm; (b) high-resolution TEM image of interface of TaN and Cu with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

from  $\langle 110 \rangle$  cross-section polycrystalline TaN/Si(100) after 700 °C annealing for 30 min (Fig. 4). The TaN layer shows up with brighter contrast compared to Si and Cu. 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 to 27 nm. The nonuniformity is due to the grain boundaries in polycrystalline TaN, which provide a faster diffusion path because the activation energy for the grain boundary diffusion is approximately half of the bulk diffusion value.<sup>14</sup>

For infinite-source-diffusion approximation, the average diffusion length of atoms can be expressed by the equation

$$C(x, \tau) = C_s \operatorname{erfc} \left( \frac{x}{2\sqrt{D\tau}} \right), \quad (1)$$

where  $C_s$  is the surface concentration,  $\operatorname{erfc}$  is the complementary error function,  $x$  is the penetration (diffusion) depth,  $D$  is the diffusion coefficient at a certain temperature, and  $\tau$  is the time for diffusion. When the argument of the complementary error function becomes unity, the concentration of copper becomes about 16% of its surface value. A rough

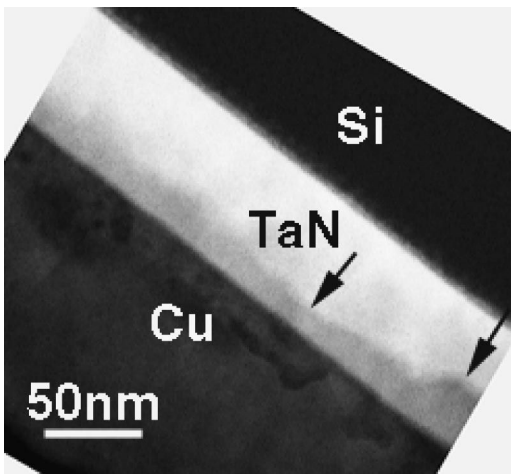


FIG. 4. STEM-Z contrast image from the  $\langle 110 \rangle$  cross-section sample of Cu on polycrystalline TaN/Si(100) after 700 °C annealing for 30 min, showing a nonuniform diffusion layer.

estimation of the 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<sup>15</sup>). The  $D$  value for 700, 650, and 600 °C were calculated to be in the range of  $10^{-16}$ – $10^{-18}$  cm<sup>2</sup>/s (see Fig. 5). According to the Arrhenius relation,  $D$  should follow the relation  $D = D_0 \exp(-Q_0/k_B T)$ , where  $Q_0$  is the activation energy of atomic diffusion. The diffusivity evaluated from Fig. 5 is  $D = (160 \pm 9.5) \exp[-(3.27 \pm 0.1) \text{ eV}/k_B T] \text{ cm}^2 \text{ s}^{-1}$ . Because in single-crystalline TaN Cu diffusion is mainly controlled by the bulk diffusion mechanism, 3.27 eV can be considered as the activation energy for bulk diffusion. 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.<sup>14</sup> Therefore,  $Q_0$  for grain-boundary diffusion is estimated to be approximately 1.6 eV, which is about six times larger than the activation energy for Cu diffusion into TiN ( $Q_0 = 0.29$  eV) by the grain-boundary mechanism reported by Lim *et al.*<sup>11</sup> This shows that TaN can be a better diffusion barrier material for Cu interconnections. Our values of activation energy compare reasonably well with the 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.<sup>16</sup> These films were deposited by a rf sputtering technique and the microstructure/defect content (which plays an important role in diffusion), was not reported.<sup>16</sup> Possible reasons for the better diffusion barrier characteristics of our single-crystal 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 ( $\sim 0.5$  nm) to explain the differences in the Cu diffusion layers between single-crystal and polycrystalline regions. Also, since pulsed-laser deposition is a nonequilibrium process, ratios of Ta/N in ablated single-crystal TaN films are determined to be  $0.95 \pm 0.05$  (determined by Rutherford backscattering spectroscopy channeling),<sup>12</sup> which is close to the stoichiometric composition. The absence of excess nitrogen vacancies in our

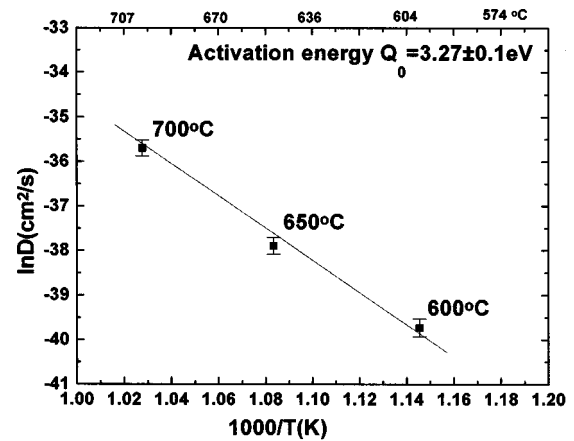


FIG. 5. Arrhenius plot showing the diffusion coefficients of Cu in a single-crystalline cubic TaN barrier layer with temperature varying from 550 to 700 °C.

samples provides more reliable values of activation energies. Furthermore, cubic TaN is a low resistivity phase compared to other TaN phases.

In conclusion, 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  $D = (160 \pm 9.5) \exp[-(3.27 \pm 0.1) \text{ eV}/k_B T] \text{ cm}^2 \text{ s}^{-1}$  from 600 to 700 °C and the results were compared with polycrystalline TaN grown directly on Si(100). This study shows that epitaxial TaN with a 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 30 min or less annealing time.

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