



## Low Temperature Physical-Chemical Vapor Deposition of Ti-Si-N-O Barrier Films

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Ti-Si-N-O films were grown by radio frequency reactive magnetron sputtering of a titanium target with nitrogen and silane gases introduced at a temperature of 40°C. X-ray diffraction and X-ray photoelectron spectroscopy results show that Ti-N, Si-N, Ti-Si, Ti-O, Si-O, and Si-N-O compounds are formed. High-resolution-transmission-electron-microscopy reveals that the film consists of Ti-N, Si-N, Ti-Si nanocrystals embedded in an amorphous Ti-O, Si-O, and Si-N-O matrix. This type of microstructure gives rise to very high stability against copper diffusion under bias temperature stressing (BTS) compared to binary barrier materials. The BTS result shows that  $Ti_{24}Si_{12}N_{35}O_{29}$  film can effectively block copper ion diffusion for up to 200°C at 0.5 MV/cm.

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It is now well recognized that future improvements in the performance of integrated circuits will depend heavily on improvements in the efficiency with which circuit elements are interconnected. Use of the Cu interconnects in microelectronic devices require development of barrier layers which can effectively prevent Cu diffusion into dielectric layers and Si substrates under the influence of electrical and thermal stresses. Extensive work in the deposition of TiN barrier film by both sputtering<sup>1,2</sup> and chemical vapor deposition<sup>3,4</sup> have been reported. A common denominator underlying many of the above references is the columnar structure of TiN, typically with a (111) or (200) preferred orientation. Such a structure can lead to short-circuit diffusion paths via grain boundaries and result in the failure of the devices. With the down-scaling of devices and more stringent reliability requirements, there is a need for more effective barrier materials. To this end, a class of refractory, ternary nitride materials, such as Ti-Si-N,<sup>5</sup> Ta-Si-N,<sup>6</sup> and W-Si-N<sup>7</sup> have been proposed as candidates for the next generation diffusion barrier in copper/low-*k* dielectric back-end-of-line device fabrication.<sup>8,9</sup> One of the advantages of these ternary barrier films is attributed to the mixed microstructure which consists of nanocrystalline M-N (M = Ti, Ta, W) embedded in amorphous matrix (Si-N).

The barrier material that we have investigated is Ti-Si-N-O films which consist of nanocrystals embedded in an amorphous matrix, but the amorphous matrix in this Ti-Si-N-O film is contributed by Ti-O, Si-O, and Si-N-O phases rather than the Si-N phase. It exhibits excellent barrier properties against Cu ion diffusion under bias-temperature stress.

In this article, we present a process for low-temperature physical-chemical vapor deposition of Ti-Si-N-O barrier films. Film composition, microstructure, and chemical bonding state have been analyzed. The barrier films showed excellent stability against bias temperature stressing (BTS), which makes them attractive candidates as future generation barrier materials.

A 630 nm thick plasma enhanced chemical vapor deposition (PECVD) SiO<sub>2</sub> layer was first deposited on a p-type silicon substrate using tetraethyl orthosilicate, [Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>] and oxygen as precursors. The deposition temperature was between 350–450°C and the pressure was 4–6 Torr. This was followed by the deposition of 215 nm Ti-Si-N-O films by radio frequency (rf) reactive magnetron sputtering of Ti target in a chamber with a base pressure of  $3.75 \times 10^{-5}$  Torr. Processing gases such as silane as a precursor, and other gases like nitrogen and argon were introduced. The pressure was maintained at  $7.1 \times 10^{-3}$  Torr during the deposition process. No substrate heating or bias were provided. The substrate tempera-

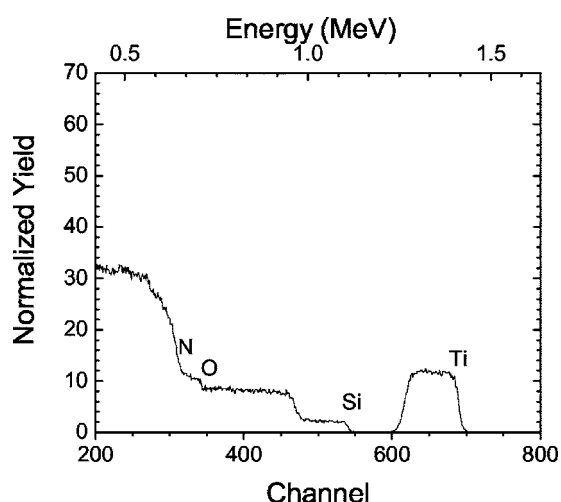
ture was measured to be 40°C when 300 W rf power was applied to the titanium target. Silane, nitrogen, and argon gas flow rates were maintained at 20, 30, and 20 sccm, respectively. Composition was obtained by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV <sup>4</sup>He<sup>+</sup> beam with the 4.0 MV Dynamitron accelerator at the Ion Beam Laboratory, Department of Physics, University of New York at Albany.

Phase composition was investigated through X-ray diffraction (XRD) using a Shimadzu XRD 6000 diffractometer. The chemical states of titanium, silicon, and nitrogen were analyzed by X-ray photoelectron spectroscopy (XPS) using 1486.71 eV Al K $\alpha$  irradiation. The X-rays and the peak positions were calibrated with respect to the C 1s peak at 284.44 eV. High resolution transmission electron microscopy (HRTEM) was used to characterize the nanostructure of the films. C–V measurements were made on a HP 4280A 1 MHz capacitance meter/C–V plotter to study the bias temperature stability of the Ti-Si-N-O films against Cu ion diffusion. A small ac signal of 10 mV rms was superposed on the applied dc bias. The Cu/Ti-Si-N-O/SiO<sub>2</sub>/Si capacitors were fabricated on Si wafers secured by vacuum chucking to an MSI Electronics light shield/hot chuck and were under nitrogen purge throughout the experiment. BTS experiments were performed at temperatures ranging from 150–200°C with a bias of 0.5 and 1 MV/cm, and biasing time of 5–90 min. The samples were biased at high temperatures, then water cooled rapidly down to room temperature (with bias on) at periodic intervals for C–V measurements.

The thickness of the Ti-Si-N-O film measured by a surface profiler was 215 nm. Although the films investigated are too thick to serve as barrier layers in current devices, in this study we focus on the microstructure and the presence of oxygen in Ti-Si-N-O layers and the resulting implication to barrier properties. Investigation of thinner layers is under investigation. The electrical resistivity for this barrier film is 3629  $\mu\Omega$  cm. According to International Technology Roadmap for Semiconductor, 2004,<sup>9</sup> when the technology node reduces from 90 to 65 nm, the required barrier thickness will reduce from 8 to 4.5 nm. With such an ultrathin barrier, electrons can tunnel through the barrier film when the current pass through the copper vias. Thus, electrical resistivity of barrier will not be a major issue for future interconnects.

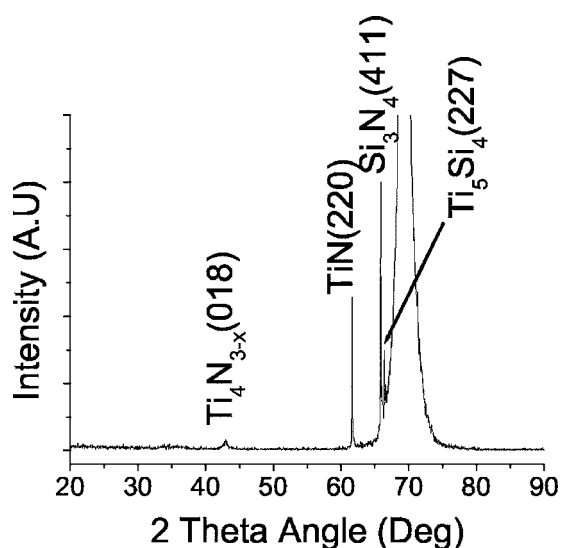
The atomic composition of the Ti-Si-N-O films was determined by Rutherford backscattering spectrometry (RBS). Figure 1 shows the backscattering spectrum of a Ti-Si-N-O/SiO<sub>2</sub>/Si sample, indicating the presence of nitrogen, oxygen, silicon, and titanium. The film contains 12 atom % of silicon when the silane gas (SiH<sub>4</sub>) flow rate was 20 sccm. The corresponding stoichiometric composition was  $Ti_{24}Si_{12}N_{35}O_{29}$ . XPS measurement shows a similar result, thus only the composition by RBS is used in the paper. In addition, XPS

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**Figure 1.** 2.0 MeV  $^4\text{He}^+$  backscattering spectrum of the Ti-Si-N-O/SiO<sub>2</sub>/Si sample. Ti-Si-N-O films were deposited at 20 sccm silane gas flow while the nitrogen gas flow rate and argon gas flow rate were maintained at 30 and 20 sccm, respectively.

further indicates the simultaneous formation of Ti-N, Si-N, Ti-Si, Ti-O, Si-O, and Si-N-O bonds when Ti 2p, Si 2p, N 1s, and O 1s peaks are deconvoluted. The presence of crystal phases, Ti-N, Si-N, and Ti-Si are further confirmed by XRD as shown in Fig. 2. Oxygen was detected throughout the thickness of the films. The presence of oxygen in the prepared barrier films could be due to the high reactivity of titanium and silicon with residual oxygen and water in the vacuum chamber. The incorporation of oxygen in TiN or Ti-Si-N film has been reported by Olowolafe et al.,<sup>10</sup> Cheung et al.,<sup>11</sup> Lempriere et al.,<sup>12</sup> Zhang et al.,<sup>13</sup> and Shtansky et al.<sup>14</sup> In the work of Shtansky et al.,<sup>14</sup> 1–5 atom % of O was found in Ti-Si-N film with a bias of –250 to 0 V during the deposition process. In the work by Olowolafe et al.,<sup>10</sup> 25 atom % of O was obtained in the deposition of TiN film in a base vacuum of  $2 \times 10^{-7}$  Torr without substrate bias. In the current work, no bias was applied to the substrate in the preparation of Ti-Si-N-O films with vacuum level of  $3.75 \times 10^{-5}$  Torr. We believe that bias will create a concentrated flux of sputtered species onto the substrate; such a high concentration prevents oxygen from getting close to the substrate surface due to pres-



**Figure 2.** XRD measurement of Ti-Si-N-O films at silane gas flow rate of 20 sccm. Ti-N, Si-N, and Ti-Si phases are detected.

sure difference. Without the bias, the oxygen in the chamber has good access to the film to react with Ti and Si, and resulted Ti-O, Si-O, and Si-N-O bonds as shown in Fig. 3.

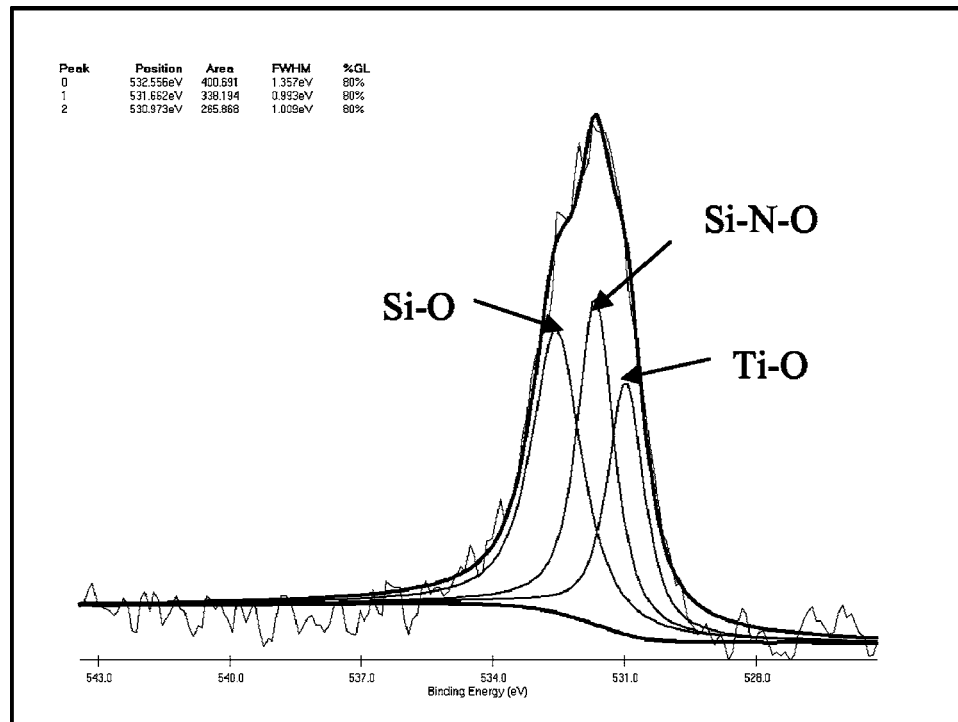
Figure 4 shows the plan view of a high resolution TEM (HRTEM) micrograph of the Ti<sub>24</sub>Si<sub>12</sub>N<sub>35</sub>O<sub>29</sub> film. It is observed that 2 to 15 nm crystals were formed with an average crystallite size of 9 nm. Combining XPS and XRD results and lattice spacing measurement from HRTEM, these nanocrystals are identified as Ti-N, Si-N, and Ti-Si phases. The remaining Ti-O, Si-O, and Si-N-O compounds are in an amorphous state.

In the work by Marcadal et al.,<sup>8</sup> nanocrystallites of TiN were reported to be embedded in amorphous Si<sub>x</sub>N<sub>y</sub> matrix. In such a configuration, fast diffusion channels were said to be absent since there was no percolation via grain boundaries in this microstructure. Reid et al.<sup>15</sup> also reported the mixed microstructure of Ti-Si-N films, and the random arrangement of the nanophase of TiN eliminates straight grain boundary paths associated with most columnar TiN films. In addition, the intergranular silicon components may be viewed as severely stuffing the grain boundaries of TiN, and thus improved the barrier performance. Similar to the work by Marcadal et al.,<sup>8</sup> the current study also produced nanocrystals embedded in an amorphous matrix. But the amorphous phases were not caused by silicon nitride any more. Si<sub>3</sub>N<sub>4</sub> was in crystalline form while the Si and Ti oxides were in an amorphous form. Apparently the formation of the oxides has significantly reduced the vitrification temperature of silicon nitride.

The barrier performance of Ti<sub>24</sub>Si<sub>12</sub>N<sub>35</sub>O<sub>29</sub> films against the Cu ions diffusion was evaluated through BTS testing. In the work of Mallikarjunan et al.,<sup>16</sup> copper was known to drift into PECVD oxide. On the other hand, when a metal insulator semiconductor (MIS) capacitor Cu/Ti<sub>24</sub>Si<sub>12</sub>N<sub>35</sub>O<sub>29</sub>/PECVD SiO<sub>2</sub>/Si was bias-temperature stressed at 150°C and 1 MV/cm for 5, 15, 30, 60, and 90 min, no flatband voltage shift was observed. In order to explore the electrical stability limit of the Ti<sub>24</sub>Si<sub>12</sub>N<sub>35</sub>O<sub>29</sub> film against Cu ion diffusion, the sample was further bias-temperature stressed at the BTS conditions of 200°C and 0.5 MV/cm. Still there was no flatband voltage shift as shown in Fig. 5. (The large negative flatband voltage that exists in the as-annealed sample is due to the presence of interface states at Ti-Si-N-O/SiO<sub>2</sub> and SiO<sub>2</sub>/Si interfaces. These interface states may be produced during processing of the films and can be reduced by annealing at 300°C in Ar–3% H<sub>2</sub> before BTS testing. With this pretreatment, the initial flatband voltage is –5 V.) This indicates that the film is stable under these test conditions, which can satisfy the BTS requirement for barrier materials. Typical computer chip operating conditions is 200°C and 0.1 MV/cm.<sup>17</sup>

So far there have been limited reports about BTS stability for ternary barrier materials. Smith et al. reported BTS results at 50 V and 200°C on 10 nm thick MOCVD TiSi<sub>x</sub>N<sub>y</sub> samples. They found that the MTF of an MOCVD Ti<sub>23</sub>Si<sub>14</sub>N<sub>45</sub>O<sub>3</sub>C<sub>3</sub>H<sub>12</sub> sample deposited at 400°C was approximately 10–100 times better than that of PVD TiN.<sup>18</sup> In general, the stability result depends on the materials, bias, testing temperature, and duration. In the work by Kizil and Steinbrüchel,<sup>19</sup> 90% barrier failure was found for amorphous TiN after 90 min BTS at 150°C under 2 MV/cm. Although amorphous TaN performed better than the TiN, 40% barrier failure still could be observed after the same BTS condition. In addition, all barriers fail more rapidly at the higher temperature, indicating that BTS stability is very sensitive to temperature rise. Based on these limited reports and our current work, ternary and quaternary barriers seem to perform better than binary system.

The reasons for the good barrier performance of the current Ti-Si-N-O system are suggested as follows: (i) stuffing of oxygen at the boundary of nanocrystals. In the work by McArthur et al.,<sup>20</sup> the improved Ti-Si-N barrier properties were believed to be due to the grain boundary stuffing of the crystallized TiN with oxygen. In our Ti-Si-N-O films, Si-N nanocrystals are formed, and these crystals can readily accommodate other atoms such as O.<sup>21</sup> Thus it is believed that O resides at the boundaries of both Ti-N and Si-N, making the diffusion of Cu ions through the grain boundaries more

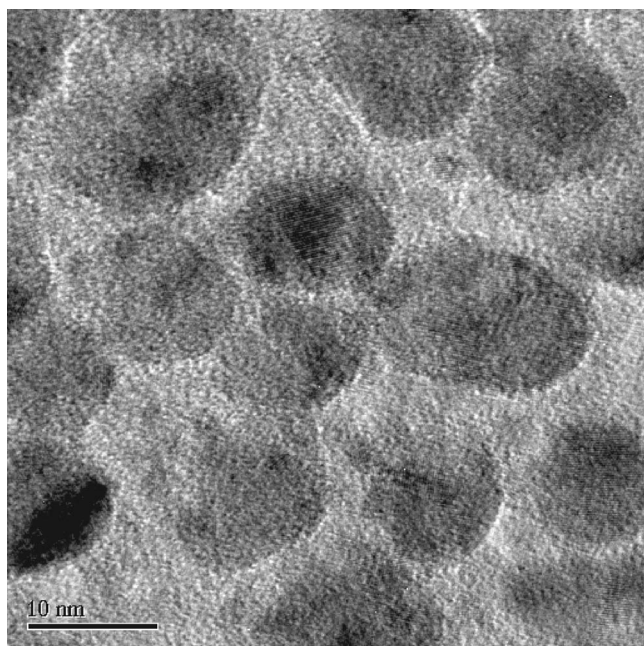


**Figure 3.** XPS analysis shows that oxygen bonded to titanium, silicon, and nitrogen forming titanium oxide, silicon oxide and silicon oxynitride when O 1s peak is deconvoluted.

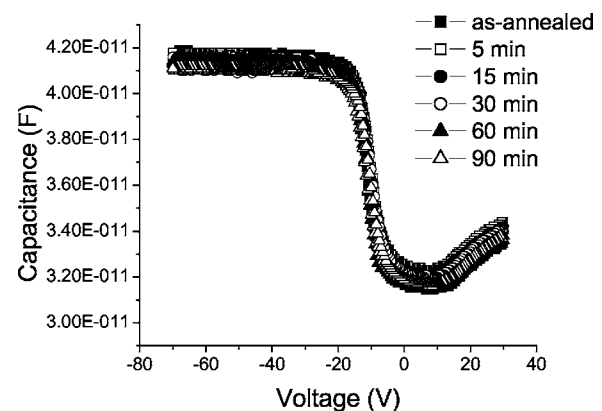
difficult. (ii) The presence of an amorphous phase reduces the density of grain boundaries. Marcadal et al.,<sup>8</sup> Eisenbraun et al.,<sup>22</sup> Joseph et al.,<sup>23</sup> Muira et al.,<sup>24</sup> and No et al.,<sup>25</sup> reported that the improved barrier properties of Ti-Si-N were related to the formation of an amorphous phase in the Ti-Si-N film. In these reports, the amorphous matrix consisted of the Si-N phase. But the amorphous matrix in our Ti-Si-N-O film is formed by Ti-O, Si-O, and Si-N-O phases. These Ti-O and Si-O bonds play an important role in the barrier performance as discussed next. (iii) Thermodynamic data<sup>26</sup> shows that the enthalpies of formation ( $\Delta H_f$ ) of Ti-O and Si-O are

–944.746 and –910.866 kJ/mol, respectively, at 300 K, compared to that of –156.057 kJ/mol for Cu-O. As reported by Mallikarjunan et al.<sup>27</sup> metals ionize when in contact with interfacial oxygen. Ionized copper may then diffuse into the dielectric under applied bias. The tendency for such a diffusion critically depends on the formation of the Cu-O bond. When Ti-O and Si-O are already present in the film before Cu deposition, the energy needed to break the Ti-O and Si-O bonds to make O available for the Cu-O bond is much higher based on the thermodynamic data. Thus the formation of Cu-O is relatively difficult and the ionization tendency of Cu is reduced with the presence of Ti-O and Si-O compounds.

In summary, a physical-chemical vapor deposition process for Ti-Si-N-O barrier was developed at 40°C. Ti-N, Si-N, and Ti-Si nanocrystals are formed and embedded in Ti-O, Si-O, and Si-N-O amorphous matrix. With this type of mixed structure, a very good electrical stability of Ti-Si-N-O film against copper ion diffusion is achieved, and it is able to prevent copper ions drifting into subsequent dielectric layers even when bias temperature stressed at



**Figure 4.** High resolution TEM reveals that the film consists of nanocrystals embedded in an amorphous matrix.



**Figure 5.** C–V plots of the MIS capacitor (Cu/Ti<sub>24</sub>Si<sub>12</sub>N<sub>35</sub>O<sub>29</sub>/PECVD SiO<sub>2</sub>/Si) that bias temperature stressed at 200°C and 0.5 MV/cm. No flat-band voltage shift is observed.

200°C and 0.5 MV/cm. These characteristics make Ti-Si-N-O an attractive candidate for future ultralarge scale integration diffusion barriers.

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