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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 Ti24Si12N35O29 film can effectively block copper ion diffusion for up to 200°C at 0.5 MV/cm.

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In the work of Olowolafe et al.,10 25 atom % of O was obtained in the deposition of Ti-Si-N-O films. The 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. 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.,10 Cheung et al.,11 Lemperiere et al.,12 Zhang et al.,13 and Shtansky et al.14 In the work of Shtansky et al.,14 1–5 atom % of O was found in Ti-Si-N film with TiN film in a base vacuum of 2 × 10−5 Torr. We believe that bias will create a concentrated flux of sputtered species onto the substrate; such a high concentration presence of crystal phases, Ti-N, Si-N, and Ti-Si is further indicated 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.,10 Cheung et al.,11 Lemperiere et al.,12 Zhang et al.,13 and Shtansky et al.14 In the work of Shtansky et al.,14 1–5 atom % of O was found in Ti-Si-N film with TiN film in a base vacuum of 2 × 10−5 Torr. We believe that bias will create a concentrated flux of sputtered species onto the substrate; such a high concentration precludes oxygen from getting close to the substrate surface due to pressure 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 Ti24Si12N35O29 film. It is observed that 2 to 15 nm crystals were formed with an average crystallite size of 9 nm. Combining XPS one 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.,8 nanocrystallites of TiN were reported to be embedded in amorphous SiN 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.17 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.,8 the current study also produced nanocrystals embedded in an amorphous matrix. But the amorphous phases were not caused by silicon nitride any more. Si3N4 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 Ti24Si12N35O29 films against the Cu ions diffusion was evaluated through BTS testing. In the work of Mallikarjunan et al.,16 copper was known to drift into PECVD oxide. On the other hand, when a metal insulator semiconductor (MIS) capacitor Cu/Ti24Si12N35O29/PECVD SiO2/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 Ti24Si12N35O29 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/SiO2 and SiO2/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% H2 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.17

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 TiSiN samples. They found that the MTTF of an MOCVD Ti24Si12N35O29C4H12 sample deposited at 400°C was approximately 10–100 times better than that of PVD TiN.18 In general, the stability result depends on the materials, bias, testing temperature, and duration. In the work by Kizil and Steinbrüchel,19 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.,20 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.21 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 1](image1.png)

**Figure 1.** 2.0 MeV He⁺ backscattering spectrum of the Ti-Si-N-O/SiO₂/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.

![Figure 2](image2.png)

**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.
The presence of an amorphous phase reduces the density of grain boundaries. Marcadal et al.,8 Eisenbraun et al.,22 Joseph et al.,23 Muira et al.,24 and No et al.,25 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 data26 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.,27 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 $200^\circ$C and $0.5$ MV/cm. No flat-band voltage shift is observed.

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.

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$_2$Si$_3$N$_5$O$_3$/PECVD SiO$_2$/Si) that bias temperature stressed at $200^\circ$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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References