Amorphous TaₓMnᵧO₂ Layer as a Diffusion Barrier for Advanced Copper Interconnects

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An amorphous TaₓMnᵧO₂ layer with 1.0 nm thickness was studied as an alternative Cu diffusion barrier for advanced interconnect. The thermal and electrical stabilities of the 1.0-nm-thick TaₓMnᵧO₂ barrier were evaluated by transmission electron microscopy (TEM) and current density–electric field (J–E) and capacitance–voltage (C–V) measurements after annealing at 400 °C for 10 h. X-ray photoelectron spectroscopy revealed the chemical characteristics of the TaₓMnᵧO₂ layer, and a tape peeling test showed that the TaₓMnᵧO₂ barrier between the Cu and SiO₂ layers provided better adhesion compared to the sample without the barrier. TEM observation and line profiling measurements in energy-dispersive X-ray spectroscopy after thermal annealing revealed that Cu diffusion was prevented by the TaₓMnᵧO₂ barrier. Also, the J–E and C–V measurements of the fabricated metal-oxide-semiconductor sample showed that the TaₓMnᵧO₂ barrier significantly improved the electrical stability of the Cu interconnect. Our results indicate that the 1.0-nm-thick TaₓMnᵧO₂ barrier efficiently prevented Cu diffusion into the SiO₂ layer and enhanced the thermal and electrical stability of the Cu interconnect. The improved performance of the TaₓMnᵧO₂ barrier can be attributed to the microstructural stability achieved by forming ternary Ta-Mn-O film with controlled Ta/Mn atomic ratio. The chemical composition can affect the atomic configuration and density of the Ta-Mn-O film, which are closely related to the diffusion behavior. Therefore, the 1.0-nm-thick amorphous TaₓMnᵧO₂ barrier is a promising Cu diffusion barrier for advanced interconnect technology.

A copper (Cu) interconnect can transmit clock and other signals for providing power/ground functions to various microelectronic devices. Cu interconnects require a liner/barrier to improve the adhesion between the Cu and silicon-based interlayer dielectric (ILD) materials and to block the diffusion of Cu into the ILD materials¹. A dual Ta/TaN barrier formed by physical vapor deposition (PVD) is generally used as a diffusion barrier as it leads to good adhesion between Cu and the ILD materials, in addition to ensuring thermal stability and blocking the diffusion of Cu into the ILD material²,³. However, the dual Ta/TaN barrier is naturally thicker than a single barrier and can increase the electrical resistivity because it occupies a larger portion of Cu line volume in the Cu interconnect. In addition, with the scaling down expected by Moore’s Law⁴, the conventional dual Ta/TaN diffusion barrier faces technological limitations⁵, including poor step coverage by PVD methods⁶ and an inability to form a barrier layer with a thickness of 1 nm or less. Recently, thinner TaN barriers prepared by atomic layer deposition (ALD) have been investigated, but their performance as barriers is not yet perfect, making them difficult to apply in practice⁷.

Instead of a dual Ta/TaN barrier which has polycrystalline structure with inherent grain boundary diffusion pathways, an amorphous TaₓO₂ barrier was investigated as a potential single barrier for Cu interconnects⁸,⁹. This oxide has a high thermal stability and is not reactive with Cu or SiO₂. Salaum et al.¹⁰ reported that a 20-nm-thick amorphous TaₓO₂ barrier showed a good performance as a diffusion barrier up to 600 °C, but it failed at higher temperatures, corresponding to the beginning of crystallization. Moreover, although amorphous TaₓO₂ layers have some advantages as diffusion barriers, a TaₓO₂ layer with a thickness less than 20 nm is not suitable for use as a Cu diffusion barrier because it is deposited as a discontinuous layer⁹.

A notable progress in Cu interconnects is a self-forming barrier proposed by Koike et al.¹⁰ The self-forming barrier was realized by spontaneously reacting the Cu–X alloying element with O and Si elements in the ILD material during post-metallization annealing¹. Among the Cu–X alloying elements used¹¹–¹⁶, an Mn alloying element¹⁷–¹⁸ is widely used because the self-formed Mn oxide or Mn silicate has good reliability and is thinner

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than the dual Ta/TaN barrier. The thickness of the self-forming barrier is determined by the temperature of post-metallization annealing and the type of deposition method, such as PVD, chemical vapor deposition (CVD), or ALD. Although the CVD method yields good step coverage, Nguyen et al. reported that it is difficult to control the barrier thickness due to the high reactivity of the Mn precursor with the SiO2 layer, and thus amorphous MnSiOx diffusion barriers with thicknesses of less than 2.0 nm are not suitable for use as Cu diffusion barriers. Moreover, the self-forming barrier is very sensitive to the processing conditions such as temperature, annealing time, and alloying concentration.

On the other hand, a MnOx layer formed by ALD was considered a good candidate because of its thickness controllability. However, it was found to act as a Cu diffusion barrier only when its thickness was greater than 1.2 nm. Furthermore, the thickness of the ALD–MnOx layer is affected by the adsorbed moisture on the substrate. The ALD–MnOx layer was very thin on the hydrophobic surface of a low-k SiOCH substrate, whereas it was thicker on a TEOS–SiO2 substrate. Thus, the surface conditions of the ILD material are very important in terms of controlling the thickness of the ALD–MnOx layer.

An alternative Cu diffusion barrier is required to meet various requirements such as good adhesion between Cu and the SiO2 layer, back-end-of-line (BEOL)-compatible deposition processes, and reliability in advanced Cu interconnects. It is desirable to avoid forming polycrystalline films with inherent grain boundaries which dominate diffusion especially at low temperatures. Therefore, the amorphous structure is still beneficial at preventing the atomic diffusion. The incorporation of an additive element in existing transition metal oxide may offer a promising method for maintaining amorphous state by interrupting the polycrystalline phase formation. In this regard, the ternary Ta-Mn-O system is of potential interest for Cu interconnects. In addition to the ability to form an amorphous structure, the electrical resistivity of the barrier layer is another important property because it has a substantial influence on the effective resistivity of the Cu interconnect, which is more affected by grain boundary scattering, surface scattering, and an increasing portion of the conventional barrier in the Cu interconnect than the resistivity of the barrier layer itself. In that sense, it is very important to minimize the thickness of the barrier layer to reduce the resistivity of the Cu interconnect. Although industry-friendly Ta-based and Mn-based barriers exhibit excellent performance in Cu interconnects, it is still challenging to fabricate a Cu diffusion barrier with a thickness less than 1.2 nm that completely prevents Cu diffusion into the ILD material.

In this study, we developed an amorphous Ta, Mn, Ox layer as an ultrathin diffusion barrier for advanced Cu interconnects that had excell’nt barrier properties, such as high thermal stability and good adhesion. A 1.0-nm-thick amorphous Ta, Mn, Ox layer was prepared by using the conventional PVD method because it allows easy and systematic investigation of the fundamental properties by changing the film thickness and chemical composition. To evaluate the thermal and electrical stability of the Ta, Mn, Ox barrier, we investigated its ability to prevent Cu diffusion into the ILD material by annealing it at 400 °C for 10 h and by applying bias thermal stress under 6 MV/cm and 150 °C for 30 min. The results of this study demonstrate that the amorphous Ta, Mn, Ox layer is a promising diffusion barrier for advanced Cu interconnects.

Results and Discussion

Figure 1a shows plan-view transmission electron microscopy (TEM) images of the as-deposited Ta, Mn, Ox barrier and selected-area electron diffraction patterns (SADPs). The Ta, Mn, Ox film was in amorphous form, as seen in the plan-view TEM image, and the SADP in the inset reveals only a halo-ring pattern, indicating a perfectly amorphous structure. The thickness of the deposited Ta, Mn, Ox barrier was determined from the cross-sectional high-resolution (HR)-TEM image as shown in Fig. 1c, and the Ta, Mn, Ox barrier was clearly distinguished between the Cu and SiO2 layer. The thickness of the barrier was 1.0 nm and it was an amorphous phase. To confirm the elemental distribution in the as-deposited MOS capacitor with the Ta, Mn, Ox barrier, the scanning TEM-electron energy loss spectroscopy (STEM-EELS) spectrum was obtained in the energy loss range for each region with Cu energy loss spectroscopy (STEM-EELS) spectrum was obtained in the energy loss range for each region with Cu.

To obtain the chemical information of the Ta, Mn, Ox diffusion barrier, X-ray photoelectron spectroscopy (XP S) analysis was performed. Figure 2 shows plan-view transmission electron microscopy (TEM) images of the as-deposited Ta, Mn, Ox barrier and selected-area electron diffraction patterns (SADPs). The Ta, Mn, Ox film was in amorphous form, as seen in the plan-view TEM image, and the SADP in the inset reveals only a halo-ring pattern, indicating a perfectly amorphous structure. The thickness of the deposited Ta, Mn, Ox barrier was determined from the cross-sectional high-resolution (HR)-TEM image as shown in Fig. 1c, and the Ta, Mn, Ox barrier was clearly distinguished between the Cu and SiO2 layer. The thickness of the barrier was 1.0 nm and it was an amorphous phase. To confirm the elemental distribution in the as-deposited MOS capacitor with the Ta, Mn, Ox barrier, the scanning TEM-electron energy loss spectroscopy (STEM-EELS) spectrum was obtained in the energy loss range for each region with Cu energy loss spectroscopy (STEM-EELS) spectrum was obtained in the energy loss range for each region with Cu. The Ta, Mn, Ox, and O layers were different in the HR-TEM image as shown in Fig. 1c, and the Ta, Mn, Ox barrier was clearly distinguished between the Cu and SiO2 layer. The thickness of the barrier was 1.0 nm and it was an amorphous phase. To confirm the elemental distribution in the as-deposited MOS capacitor with the Ta, Mn, Ox barrier, the scanning TEM-electron energy loss spectroscopy (STEM-EELS) spectrum was obtained in the energy loss range for each region with Cu energy loss spectroscopy (STEM-EELS) spectrum was obtained in the energy loss range for each region with Cu.

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To obtain the chemical information of the Ta, Mn, Ox diffusion barrier, X-ray photoelectron spectroscopy (XPS) analysis was performed and the results are shown in Fig. 2. The experimental XPS spectra were deconvoluted using Gaussian-Lorentzian peaks after background extraction. As shown in Fig. 2a, the Ta 4f spectrum revealed that Ta 4f1/2 and Ta 4f3/2 existed at peak values of 25.8 eV and 27.7 eV, respectively, and the loss feature for Ta, Ox appeared at 36.8 eV. These peaks corresponded to the binding energy of fully oxidized stoichiometric Ta2O5, which was in good agreement with previous work. 26,29. Fig. 2b shows the XPS spectrum of Mn 2p in the Ta, Mn, Ox diffusion barrier. The main two peaks with binding energies at 641.2 eV and 653.4 eV corresponded to Mn 2p3/2 and Mn 2p1/2, respectively. Peak fitting was conducted for Mn 2p3/2, which was deconvoluted into Mn2+, Mn3+, and Mn4+, with characteristic binding energies at 640.7 eV, 641.8 eV, and 643.1 eV, respectively. The Mn 2p1/2 peak also demonstrated an MnO satellite feature at 646.2 eV. The Mn metal in the Ta, Mn, Ox barrier consisted of MnO, MnO2, and Mn2O3, based on the obtained binding energy at the Mn 2p3/2 peak. In Fig. 2c, there were three O 1s peaks at 530.1 eV, 531.2 eV, and 532.9 eV, indicating metal–oxide (M–O), metal–oxygen vacancy (M–Ovac), and metal–hydrogen lattice (M–OH) bonds, respectively. The M–O, M–Ovac, and M–OH bonds were formed by binding with the Ta and Mn metals in the Ta, Mn, Ox diffusion barrier.

Because the rough surface of the diffusion barrier can provide a fast diffusion pathway for Cu migration across the liner, the surface roughnesses of the 1.0-nm-thick Ta, Mn, Ox barrier and the SiO2 layer without the barrier (reference) were measured using atomic force microscopy (AFM). A smooth surface with a root mean square (RMS) value of 0.20 nm was obtained for the 1.0-nm-thick Ta, Mn, Ox barrier, which was similar to the RMS of the
10-nm-thick SiO\textsubscript{2} layer (0.19 nm), as shown in Fig. 3a,b. To examine the Cu adhesion to the SiO\textsubscript{2} surface resulting from the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier, 3 M Scotch tape peeling tests were performed for the MOS capacitor samples with and without the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier. As shown in Fig. 4a,b, the MOS capacitor sample without the barrier failed the tape peeling test owing to poor adhesion, which was apparent from the removal of the Cu dot electrodes. In contrast, for the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier sample, the Cu dot electrodes deposited on the SiO\textsubscript{2} layer did not change after the tape peeling test, as shown in Fig. 4c,d, despite multiple attempts to tear off the Cu dot electrodes. These results indicate that the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier had good adhesion between the Cu and SiO\textsubscript{2} layers.

To investigate the thermal stability of the 1.0-nm-thick Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier, we annealed the MOS capacitor samples with and without the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier at 400 °C for 10 h. Figure 5 shows the cross-sectional HR-TEM images and the line profile of the chemical composition for each element after annealing at 400 °C for 10 h. To compare the results with and without the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier, a MOS capacitor sample without a barrier was
prepared as a reference. For the sample without the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier, the interface between the Cu and SiO\textsubscript{2} layer showed a noticeable difference because of Cu diffusion into the SiO\textsubscript{2} layer during annealing, as shown in Fig. 5a.

The initial SiO\textsubscript{2} layer with a thickness of 10 nm was reduced to approximately 5.8 nm owing to Cu diffusion. Conversely, the annealed sample with the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier was identical to the initial interface between the Cu and SiO\textsubscript{2} layers and had a uniform thickness of 1.0 nm, which was consistent with the as-deposited Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier before annealing, as shown in Fig. 5b,c. In addition, the STEM-energy dispersive X-ray spectroscopy (STEM-EDS) line profile, shown in Fig. 5d,e, was used to accurately evaluate the Cu diffusion. For the sample without the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier (see Fig. 5d), Si and O were detected in the SiO\textsubscript{2} layers, as shown in the high-angle annular dark-field (HAADF) STEM image, and the distribution of Cu showed that the Cu atoms diffused into the SiO\textsubscript{2} layer. The annealed Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} diffusion barrier showed the same chemical binding states as the as-deposited Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier, as shown in Fig. S1 of the SI. In the STEM-EDS line profile of the annealed sample with the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier shown in Fig. 5e, Cu was not detected inside the SiO\textsubscript{2} layer, which indicated no diffusion of Cu into the SiO\textsubscript{2} layer. However, the Ta and Mn in the diffusion barrier were not properly detected in the barrier region between the Cu and the SiO\textsubscript{2} layers, despite the presence of the Ta\textsubscript{x}Mn\textsubscript{y}O\textsubscript{z} barrier. In fact, the quantitative analysis using STEM-EDS for Ta in the MOS capacitor sample was difficult because the Ta M\textalpha\textsubscript{K} (1.71 keV) and Ta L\textalpha\textsubscript{K} (8.14 keV) X-ray energies overlapped with the Si K\textalpha\textsubscript{K} (1.74 keV) and Cu K\textalpha\textsubscript{K} (8.04 keV) X-ray energies, respectively. In addition, Mn was difficult to detect in the line profile owing to the damage caused by the 200-keV e-beam during the STEM-EDS analysis. To complement STEM-EDS, Ta and Mn were confirmed using STEM-EELS. As shown in Fig. 5f, Ta and Mn were detected at the interface between the Cu and SiO\textsubscript{2} layers. In
addition, the Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> barrier prevented the diffusion of Cu toward the SiO<sub>2</sub> layer, which was consistent with the Cu distribution in the STEM-EDS line profile. However, the detection of trace elements that may have affected the device characteristics was difficult because the detection limits of STEM-EDS and -EELS are approximately 0.1–3.0 wt.%<sup>34</sup>. Therefore, to determine the presence of a few Cu atoms in amounts as low as 10<sup>9</sup> atoms/cm<sup>3</sup><sup>35</sup>, the current density-electric field (<i>J–E</i>) and capacitance-voltage (<i>C–V</i>) characteristics were evaluated.

Figure 6 shows the dielectric breakdown field of a statistical time-zero dielectric breakdown (TZDB) histogram obtained using 20 <i>J–E</i> curves, as shown in the inset of Fig. 6 for the as-deposited and annealed MOS capacitor samples. In the statistical results of the TZDB histogram, three modes, referred to as A-, B-, and C-modes, were observed when the breakdown fields were composed of low (<1 MV/cm), intermediate, and high (>14 MV/cm) fields, respectively<sup>36</sup>. The A- and B-mode failures could be attributed to localized defect spots, such as Cu<sup>+</sup> ion transport, referred to as an extrinsic breakdown, and the C-mode failure corresponded to an approximately defect-free oxide sample, referred to as an intrinsic breakdown. As shown in Fig. 6a,b, the MOS capacitor sample without the barrier exhibited the C-mode failure ranging from 14.25 MV/cm to 16.25 MV/cm before annealing, whereas the A- and B-mode failures ranged from 3.25 MV/cm to 12.25 MV/cm after annealing at 400 °C for 10 h. Thus, the MOS capacitor sample without the barrier exhibited extrinsic breakdown because of the Cu<sup>+</sup> ions that diffused into the SiO<sub>2</sub> layer during annealing. Conversely, in Fig. 6c,d, the Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> barrier samples exhibited C-mode failure regardless of annealing, unlike the reference sample without the barrier, and the breakdown field before and after thermal annealing ranged from 15.45 MV/cm to 16.95 MV/cm and from 15.55 MV/cm to 16.55 MV/cm, respectively. These results provide evidence that the penetration of Cu<sup>+</sup> ions into the SiO<sub>2</sub> layer did not occur, which is consistent with the TEM results shown in Fig. 5.

In addition, a correlative analysis of the XPS and <i>J–E</i> measurements was carried out to evaluate the performance of the 1.0-nm-thick Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> barrier layer according to the content of Ta and Mn. The Ta/Mn ratio (i.e., the normalized chemical composition of the metals) of the as-deposited Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> layer was estimated by the wide-scan XPS survey spectra, and the TZDB histogram was measured to evaluate the Cu-blocking capability of the Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> barrier after annealing at 400 °C for 10 h. Three 1.0-nm-thick Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> barriers, each with a different Ta/Mn ratio, were prepared by controlling only the deposition time during DC sputtering. As shown in Fig. S2 of the SI, the 1.0-nm-thick Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> barrier with a normalized Ta content of 91.5% (balance Mn) could not completely block Cu diffusion into the SiO<sub>2</sub> layer during annealing. Conversely, for the Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> barrier with normalized Ta content range from 56.5% to 62.6%, the TZDB results showed that the penetration of Cu<sup>+</sup> ions into the SiO<sub>2</sub> layer did not occur. Therefore, the chemical composition (Ta/Mn ratio) can affect the performance of Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub> barrier. The incorporation of an additive element in existing binary system can lead to a change in atomic configuration and density of the barrier and contribute to maintain a high thermal stability by suppressing the polycrystalline phase formation<sup>37–39</sup>. Fig. S3 of the SI shows the detailed Ta 4f XPS spectrum of Ta<sub>x</sub>Mn<sub>y</sub>O<sub>z</sub>.
barrier with the normalized Ta content of 91.5% in Fig. S2a. This deconvoluted Ta 4f XPS spectrum revealed that the Ta 4f7/2 and 4f5/2 binding energies corresponded to the metallic Ta as well as the amorphous Ta2O5, unlike TaₓMnᵧOz barrier containing the normalized Ta content of 46.55% (Fig. 2a). Therefore, the poor barrier property of the TaₓMnᵧOz layer with a high Ta/Mn ratio can be attributed to a lack of Mn and O atoms to bind Ta and the presence of metallic Ta atoms. Bassiri et al. reported that the Ta-Ta and Ta-O bonding distances were determined as 3.1 Å and less than 2 Å, respectively, by analyzing high-quality EXAFS spectra of ion beam sputtered amorphous tantala. This implies that the amount of Ta-Ta and Ta-O bonds is closely related to the atomic configuration and density of the TaₓMnᵧOz film. Therefore, the performance of 1.0 nm-thick TaₓMnᵧOz barrier can be affected by the binding states between Ta, Mn and O, depending on the Ta/Mn ratio.

The normalized C–V characteristics of MOS capacitor samples with and without the TaₓMnᵧOz barrier upon annealing at 400 °C for 10 h are shown in Fig. 7. In Fig. 7a, the MOS capacitor sample without the barrier shows a negative flatband voltage shift (indicated by the green arrow) from −0.94 V to −2.54 V upon annealing owing to Cu⁺ ion transport into the SiO2 layer, which indicates a buildup of positive charge within the SiO2 layer during annealing. In addition, the hysteresis in the C–V curve indicates movement of the Cu⁺ ion within the dielectric film during the C–V sweep. It was noted that the flatband voltage of the MOS capacitor with the TaₓMnᵧOz barrier before annealing was more negative than that of the as-deposited reference sample without the TaₓMnᵧOz barrier (Cu/SiO2/Si). This can be attributed to intrinsic defects (positive charge was calculated as 4.63 × 10⁻¹¹ C) such as charges in SiO2 or oxygen vacancies in the TaₓMnᵧOz layer. The flatband voltage moved to the positive region from −2.25 V to −0.49 V (indicated by the purple arrow) upon annealing owing to the removal of the intrinsic defects in the MOS capacitor sample and not from the diffusion of Cu⁺ ions into the SiO2 layer. In other words, there was no flatband voltage shift toward the negative region, and no hysteresis curve was observed in the MOS capacitor with the TaₓMnᵧOz barrier, as shown in Fig. 7b, indicating that the Cu⁺ ions were effectively prevented from diffusing into the SiO2 layer by the TaₓMnᵧOz barrier.

The normalized C–V characteristics before and after bias thermal stress (BTS) were also measured. Figure 8 shows the normalized C–V curves for MOS capacitor with and without the TaₓMnᵧOz barrier after BTS at 6 MV/cm and 150 °C for 30 min. As shown in Fig. 8a, for the MOS capacitor without a barrier, the normalized C–V curve presented a roughly −1.0 V observable shift of flatband voltage toward the negative region under an electrical field of 6 MV/cm, which is consistent with the normalized C–V sweep after thermal annealing. Conversely,
the MOS capacitor with the Ta,Mn,O3 barrier showed no negative shift in flatband voltage, as shown in Fig. 8b. A positive shift of flatband voltage in the C–V curve occurred because of the removal of intrinsic defects during annealing.

Consequently, these results provide direct evidence that the 1.0-nm-thick amorphous Ta,Mn,O3 layer is suitable for use as an ultrathin diffusion barrier that can improve the reliability and lifetime of advanced Cu interconnects.

**Conclusions**

We investigated the effectiveness of an amorphous Ta,Mn,O3 layer as an ultrathin diffusion barrier for advanced Cu interconnects. A 1.0-nm-thick Ta,Mn layer was oxidized by exposure to air to obtain an amorphous Ta,Mn,O3 film. Ta and Mn were present as Ta2O5, MnO, MnO2, and Mn2O3 in the amorphous Ta,Mn,O3 film. The tape peeling test for the MOS capacitor sample showed no delamination in the presence of the Ta,Mn,O3 layer, which improved the adhesion between the Cu and the SiO2 layers. To evaluate the diffusion barrier properties of the 1.0-nm-thick amorphous Ta,Mn,O3 film, MOS capacitor samples with and without the barrier were annealed at 400 °C for 10 h. HR-TEM and STEM-EDS/EELS analyses showed that the amorphous Ta,Mn,O3 barrier had a stable microstructure and chemical composition, even after thermal annealing. The J–E, C–V and TZDB results showed that the diffusion of Cu was effectively blocked by the amorphous Ta,Mn,O3 barrier. The correlative analysis of XPS and TZDB revealed that, with a comparable O concentration, the Ta/Mn atomic ratio affected the atomic configuration and density of Ta–Mn–O films. To prevent the Cu diffusion into the Ta–Mn–O film, the Ta/Mn ratio needs to be high to ensure a high atomic density. However, the Ta/Mn ratio cannot be too high because a lack of Mn and O atoms to bind Ta and the presence of the metallic Ta atoms deteriorates the barrier performance. In conclusion, a 1.0-nm-thick amorphous Ta,Mn,O3 layer serves as an adhesion promoter and excellent diffusion barrier, and it can be used as a single liner/barrier material for advanced Cu interconnects.
Methods

The substrates for barrier deposition were 10-nm-thick SiO$_2$ films on p-type doped silicon (100) wafers and were cleaned using a piranha solution of 3:1 sulfuric acid (H$_2$SO$_4$) and hydrogen peroxide (H$_2$O$_2$). Then, the Mn layer was deposited first, followed by Ta layer deposition of the Mn/SiO$_2$/Si substrate by direct current (DC) magnetron sputtering using a Mn target (purity 99.9%) and Ta target (purity 99.9%) under a power of 5W at an Ar gas pressure of 5.5 mTorr (see Fig. S4 of the SI for the deposition process and the formation of the Ta$_3$Mn$_2$O$_7$ layer). The DC sputtering chamber was pumped down to a base pressure less than 4.0 $\times$ 10$^{-7}$Torl and pre-sputtering was conducted at 10 W higher than the processing power for 20 min before deposition. The sequentially deposited ultrathin Mn and Ta films were intermixed to form a Ta$_3$Mn$_2$ film. The 1.0-nm-thick Ta$_3$Mn$_2$ film was oxidized by atmospheric exposure for the ex-situ sputtering to deposit the Cu film. Fig. S4 of the SI shows a schematic of the oxidation mechanism of the Ta$_3$Mn$_2$ film. The oxidized Ta$_3$Mn$_2$ film is referred to as the Ta$_3$Mn$_2$O$_7$ layer. It was found that this intermixing and oxidation mechanism was valid only for sequentially deposited ultrathin Mn and Ta films with a total thickness less than 2.5 nm (see Fig S5 of the SI).

To fabricate the MOS capacitor structure, 150-nm-thick Cu films were then deposited on the Ta$_3$Mn$_2$O$_7$ film by DC magnetron sputtering with dots of 100 µm diameter through a shadow mask, and a 50-nm-thick Ta film was coated as the capping layer. MOS capacitor samples with and without the 1.0-nm-thick Ta$_3$Mn$_2$O$_7$ layer were prepared using the same deposition method. To evaluate the thermal stability of the Ta$_3$Mn$_2$O$_7$ layer as a diffusion barrier, the as-deposited MOS capacitor samples were annealed at 400°C for 10 h in a tube furnace under Ar + 10% H$_2$ gas flow. XPS (ESCALAB250Xi, Thermo-Scientific, UK) was used to determine the chemical characteristics of the deposited Ta$_3$Mn$_2$O$_7$ layer. Samples for cross-sectional transmission electron microscopy (TEM) were fabricated using a focused ion beam (FIB, NXX2000, Hitachi). The TEM samples were milled using a high-energy Ga$^+$ ion beam from 30 keV to 5 keV and a low-energy Ar$^+$ ion beam of 1 keV after the electron beam-induced deposition of the W material as a protective layer to minimize damage to the surface layers during the FIB milling process$^{44,45}$. TEM (JEOL ARM-200F) analysis at 200 kV with EDS and EELS were used to analyze the microstructure and to obtain the line profiles for the chemical composition of the Cu, Ta, Mn, Si, and O elements in the two types of samples before and after annealing. The surface morphology of the 1.0-nm-thick Ta$_3$Mn$_2$O$_7$ layer was analyzed by AFM (Park System Co.), and the adhesion strength between the Cu and SiO$_2$ layers depending on the presence of the Ta$_3$Mn$_2$O$_7$ barrier was examined using a 3M Scotch tape peeling test$^{46}$.

To evaluate the Cu diffusion barrier performance of Ta$_3$Mn$_2$O$_7$ after annealing at 400°C for 10 h, the J–E characteristics were evaluated using a microprobe system connected to an Agilent B1500A parametric analyzer. The J–E curves were measured by applying voltage ranging from 0 V to −20 V in −50-mV steps. The BTS tests were performed by using a microprobe system capable of annealing and applying a high electric field to the MOS capacitor in a controlled environment. For the BTS tests, a bias field of 6 MV/cm was applied on the MOS capacitor at 150°C for 30 min. After a given time period, the samples were cooled to room temperature. The C–V characteristics before and after thermal annealing and BTS were evaluated using a probe station with an Agilent E4980A precision LCR meter with an AC frequency of 100 kHz. For all C–V measurements, a voltage ranging from +4 V to −4 V was applied in 0.1-V steps, and the hysteresis was scanned by applying a reverse voltage of −4 V to +4 V.

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Competing interests
The authors declare no competing interests.

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