Comparative study of ZrN and Zr–Ge–N thin films as diffusion barriers for Cu metallization on Si

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The diffusion barrier properties of Zr–Ge–N and ZrN thin films for Cu metallization on Si have been examined. Both Zr–Ge–N and ZrN thin films deposited at room temperature via reactive magnetron sputtering are amorphous. X-ray diffraction of annealed Cu/nitride/Si structures indicates that a 50 nm thick ZrN film is an effective diffusion barrier for annealing at 600 °C for 1 h. In contrast, Zr–Ge–N failed as a diffusion barrier upon annealing at 600 °C as evidenced by the appearance of copper silicide diffraction peaks. Cross-section transmission electron microscopy also showed the formation of Cu3Si crystallites at the annealed Zr–Ge–N barrier interfaces. For ZrN barriers annealed at 600 °C, the integrity of the nitride/Si interface is preserved and the energy-dispersive spectrometry line scan showed no Cu diffusion through the barrier into Si substrate. The result indicated that ZrN is superior to Zr–Ge–N as a copper diffusion barrier on Si. © 2008 American Vacuum Society. [DOI: 10.1116/1.2976571]

I. INTRODUCTION
The formation of barrier layers is important when integrating chemically incompatible materials. This is evident for a number of electronic applications,1,2 most notably semiconductors.3 As device and circuit dimensions continue to shrink, the interconnect delay is becoming increasingly important in determining the device and circuit performance. Copper metallization is replacing aluminum for IC interconnects due to its lower resistivity and better electromigration properties under high current densities.4 However, there remains significant challenges in copper integration. Cu diffuses rapidly into Si, SiO2, and Ge even at low temperature. Cu is known to form deep level traps in silicon (acceptor levels at 0.24, 0.37, and 0.52 eV above the valence band). When Cu diffuses into Ge and resides on a substitutional site, it introduces three acceptor levels that are located 0.04 and 0.32 eV above the valence band and 0.26 eV below the conduction band.6 Therefore the introduction of a barrier layer is required between Cu and the underlying dielectric to prevent the diffusion of copper into the semiconductor or dielectric materials. Another function of the barrier layer is to provide good adhesion, in particular, to the dielectric materials, since copper has poor adhesion to most dielectrics.7

Single crystal diffusion barriers would be ideal for diffusion barriers due to a lack of diffusion pathways through grain boundaries. While the growth of epitaxial barriers has been employed in some electronic material applications,8 it is not practical for metal interconnects on Si due to process restrictions and material properties including a limited thermal budget and lattice mismatch. An amorphous structure barrier is therefore preferred due to the lack of grain boundaries. Refractory metal nitrides such as TiN,10–13 TaN,14–16 and WNx (Refs. 17–20) are being studied intensely as diffusion barriers for Cu metallization. Unfortunately diffusion barriers of these materials often fail at relatively low temperature due to recrystallization. By introducing a third element into refractory metal nitrides, one can amorphorize the crystalline phases and increase the recrystallization temperature, thereby increasing the robustness of the diffusion barrier. The addition of Ge as well as Si to the matrix should enhance the material’s resistance to recrystallization with potential improvement in diffusion performance. Some of the ternary nitride systems that have been studied include Ta–Si–N, W–Si–N, and W–Ge–N.21–25

Like most refractory metal nitrides, ZrN has a high melting temperature of 2960 °C. The lowest electrical resistivity reported in bulk for ZrN is 13.6 μΩ cm.26 The standard heat of formation of ZrN at 298 K, ΔHf = −87.3 kcal/mol,27 is more exothermic than those of TiN (−80.4 kcal/mol) and TaN (−60.3 kcal/mol), suggesting greater thermodynamic stability of the ZrN compound as compared to other refractory metal nitrides. The aforementioned properties make it an interesting barrier material for copper diffusion with excellent barrier performance.28–31 For example, Sato et al. demonstrated the effectiveness of 5 nm N-rich ZrN thin film as a diffusion barrier upon annealing at 500 °C for 30 min.31 In this article, we compare the diffusion barrier properties of ZrN and Zr–Ge–N for copper metallization on Si.

II. EXPERIMENTAL PROCEDURES
ZrN and Zr–Ge–N films were deposited on Si (100) wafers via magnetron sputtering at room temperature. A stoichi-
omeric ZrN target was used for ZrN film growth. The Zr–
Ge–N samples were prepared by cosputtering of ZrN and Ge
targets. Prior to deposition, the substrate was etched in 7:1
buffered oxide etch to remove native oxide, followed by de-
ionized water rinse. The base pressure of the chamber was on
the order of $5 \times 10^{-7}$ Torr. Before deposition, the sputtering
targets were presputtered at an Ar gas pressure of 15 mTorr
for 10 min. The forward sputtering powers for ZrN and Ge
were 200 and 100 W, respectively. Nitride film deposition
was carried out at a fixed Ar pressure of 10 mTorr. During
the deposition the substrates were rotated at 20 rpm to ensure
film uniformity.

After deposition of the nitride films, a 200 nm thick Cu
layer was deposited on the barrier in situ at room temperature
without breaking the vacuum. The forward sputtering power
for Cu deposition was 200 W. The chamber pressure was
kept at 5 mTorr Ar throughout the process. Diffusion barrier
properties were examined by annealing the structure in
vacuum at a base pressure less than $10^{-5}$ Torr over the tem-
perature range of 400–700 °C for 1 h. The film crystallinity
and intermetallic phase formation were determined using a
Philips APD 3720 x-ray diffractometer (XRD). The integrity
of the stack films and chemical depth profile of Cu through
the diffusion barrier were evaluated using a JEOL 2010F
high resolution transmission electron microscope (HRTEM)
along with a JEOL Superprobe 733 energy-dispersive spec-
trometer (EDS). The surface morphology of the films was
determined using JEOL 6400 scanning electron microscopy
(SEM). For characterization of electrical properties, a four
point probe was used to measure the sheet resistance of the
Cu layer.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns for as-
deposited and annealed ZrN and Zr–Ge–N barrier stacks
with a thickness of 50 nm. ZrN and Zr–Ge–N films depos-
it at room temperature were amorphous as evidenced by
the lack of associated diffraction peaks in the x-ray diffrac-
tion patterns. This amorphous phase is a desirable micro-
structure for diffusion barrier applications and is also present
in thicker ZrN and Zr–Ge–N films. After high temperature
annealing of the barrier stacks, the crystallinity of Cu had
increased as indicated by the stronger and sharper Cu (111)
and Cu (200) peaks. The ZrN barrier stack remained intact
upon annealing at 600 °C for 1 h. Further annealing at
higher temperature led to copper diffusion through the ZrN
into Si and the formation of copper silicide [Fig. 1(a)]. Note
that no ZrN diffraction peaks were evident at failure tem-
peratures, possibly because the amount of barrier material
was below the detection limit for XRD. Nevertheless, failure
of the barrier upon annealing at temperature $>$600 °C is
consistent with undetectable amounts of recrystallization,
as the formation of grain boundaries would provide fast diffu-
sion paths for Cu. In contrast, the diffraction pattern for the
Zr–Ge–N barrier stack remains unchanged upon annealing at
500 °C for 1 h [Fig. 1(b)]. After 600 °C annealing, however,
noticeable copper silicide peaks appeared as a result of cop-
per diffusion, indicating barrier failure.

The surface morphology of the stack films was evaluated
by scanning electron microscopy. For Cu/ZrN/Si stack
samples, the Cu grain structure was coarsened after higher
temperature annealing. There is no evidence of delamination
or the presence of copper silicide crystallites after annealing
at 600 °C. In comparison, the surface morphology of Cu/Zr–
Ge–N/Si stack samples annealed at 500 and 600 °C
is shown in Fig. 2. Similar to the Cu films on ZrN, the Cu
films are continuous on the Zr–Ge–N barrier after annealing
at 500 °C. Noticeable copper silicide crystallites appeared
after annealing at 600 °C: copper silicide was also evidenced
by XRD patterns. The lower failure temperature of Zr–Ge–N
could be attributed to the reaction of Cu with Ge, although
there was no evidence of copper germanide within the detect-
ance limit for XRD. The Ge concentration might exceed its
solubility limit in the ZrN matrix and cause Ge segregation
in the films resulting in some changes in its structural
properties. Krusin-Elbaum and Aboelfotoh reported that
Cu reacts readily with Ge to form a stable copper germanide \( \varepsilon - \text{Cu}_3\text{Ge} \) phase at low temperature. The failure mechanism of Zr–Ge–N films could be the formation of structural defects as a result of reaction of Cu and segregated Ge at the Cu/Zr–Ge–N interface. These defects could facilitate the diffusion of Cu into Si as well as the transport of Si across the barrier to form copper silicide.

The interface integrity of the barrier stack was examined by cross-section transmission electron microscopy (XTEM). Figure 3 shows the XTEM images of as-deposited and 600 °C annealed ZrN barrier stacks. The interface integrity of the ZrN barrier before and after annealing at 600 °C shows essentially no difference, consistent with the XRD data in which no copper silicide peak appears. The ZrN layer is uniform in thickness and the interfaces of Cu/ZrN/Si are sharp and uniform after annealing, indicating that this system is thermally stable to 600 °C for 1 h. Note that the texture of as-grown ZrN was amorphous and became nanocrystalline after annealing, which effectively blocks copper diffusion. In contrast, Cu diffusion is clearly seen in Zr–Ge–N films annealed at 600 °C as evidenced by the formation of Cu$_3$Si crystallites at the interface Fig. (4(b)). The thick black layer on top of Cu is Pt, which functions as a protective layer when preparing XTEM samples via focused ion beam milling. The chemical depth profiles (EDS) for the stack films before and after annealing were also examined. Figure 5 shows the Cu diffusion depth profile for a ZrN barrier stack before and after annealing at 600 °C for 1 h. Before annealing, the Cu signal declines sharply before the Si substrate can be detected. Similarly, after annealing, the Cu signal also returns to its baseline before reaching the ZrN/Si interface, although a small amount of Cu did penetrate into the ZrN layer. Nevertheless, the Cu signal was undetectable before the scan moved into the Si substrate, indicating no Cu diffusion into Si.

The sheet resistance of the Cu on the nitride barriers was measured via a standard four point probe, as shown in Fig. 6. Before the barriers started to fail, the Cu sheet resistance decreased with heat treatment for both ZrN and Zr–Ge–N systems due to Cu grain growth. For the ZrN system, the sheet resistance of Cu increased rapidly upon annealing at 600 °C, indicating the onset of the failure process via formation of more resistive copper silicide. Likewise, the Cu sheet...
resistance on Zr–Ge–N system began to increase at 500 °C, also revealing the onset of barrier failure. The electrical behavior is thus consistent with the previously described microstructure changes.

IV. CONCLUSIONS

In conclusion, the copper diffusion barrier properties of Zr–Ge–N on Si have been examined and compared to ZrN. A 50 nm thick Zr–Ge–N barrier was shown to prevent Cu diffusion at 500 °C for 1 h, as evidenced by the lack of copper silicide peaks in the x-ray diffraction patterns. The ZrN barrier film was a more thermally stable as it prevented Cu diffusion to 600 °C for 1 h. SEM and TEM both showed the onset of formation of copper silicide crystallites for Zr–Ge–N barriers annealed at 500 °C. In contrast, XTEM on a ZrN barrier annealed at 600 °C revealed sharp interfaces and showed no intermetallic compound formation. The Cu atomic depth profile on XTEM sample indicated no interdiffusion across the ZrN barrier layer. Before barrier failure, the Cu sheet resistance for both systems decreased with increased annealing temperature due to Cu grain growth, followed by an increase due to the formation of more resistive copper silicide. Overall, the results showed that ZrN is a superior diffusion barrier as compared to Zr–Ge–N for copper metallization on Si.

Fig. 4. Cross-section HRTEM images of Cu/Zr–Ge–N(50 nm)/Si (001) (a) as-deposited and (b) annealed at 600 °C for 1 h.

Fig. 5. EDS depth profile of Cu/ZrN(50 nm)/Si for (a) as-deposited Cu signal, (b) as-deposited Zr signal, (c) as-deposited Si signal, (d) 600 °C annealed Cu signal, (e) 600 °C annealed Zr signal, and (f) 600 °C annealed Si signal.

Fig. 6. Sheet resistance of Cu vs annealing temperature for Cu/ZrN/Si and Cu/Zr–Ge–N/Si.
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