Properties of W–Ge–N as a diffusion barrier material for Cu

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The properties of W–Ge–N thin films are reported, focusing on issues relevant to their use as diffusion barriers for Cu metallization on silicon. The amorphous W–Ge–N thin films were deposited on thermally grown SiO2/Si using reactive sputter deposition. This was followed by in situ deposition of Cu films. Annealing studies for W–Ge–N were then carried out in a vacuum to investigate Cu diffusion and barrier film crystallization. X-ray diffraction was used to assess the crystallinity of the films upon annealing. The results show that W–Ge–N has a recrystallization temperature that is higher that that for WNx. Auger electron spectroscopy was used to measure the depth profile of Cu diffusion through the barrier layer. Little or no Cu diffusion was detected for a relatively high annealing temperature. The W–Ge–N films were conductive, although the resistivity is somewhat higher than that for WNx. The results suggest that W–Ge–N may be an attractive diffusion barrier material for Si or SiGe devices. © 2005 American Institute of Physics.

For present and future integrated electronic technologies, the use of barrier materials to enable materials integration is increasingly important. In current Si technology, the push for higher circuit density and low resistance/capacitance time delays has made copper the material of choice for interconnects due to its higher resistance to electromigration and lower resistivity as compared to Al. Unfortunately, Cu shows poor adhesion to most dielectric materials and rapidly diffuses into SiO2 and Si. This obviously degrades the electrical properties of devices, creating the need for intermediate layers that provide a barrier to Cu diffusion.

When considering the role of microstructure in diffusion processes, amorphous materials are generally better suited than polycrystalline phases, as grain boundaries provide high diffusivity pathways for Cu diffusion through the barrier material. Among the material systems currently being developed, binary nitrides, such as TaN (Refs. 2 and 3) and WNx,4,5 are receiving significant attention. For Ta-based barriers, the Ta–Cu phase diagram indicates that Ta and Cu are effectively immiscible even at their melting temperature. Unfortunately, recrystallization of TaN films occurs at approximately 600 °C, which is relatively low for diffusion barrier applications. WNx is also an interesting candidate as it is relatively easy to synthesize as an amorphous film. In this case, the nitrogen content in WNx films has a significant influence on its diffusion barrier properties. For WNx films with low nitrogen content, the recrystallization temperature can be on the order of 450 °C.6 Higher nitrogen content yields higher recrystallization temperature. Yet, the primary mode of failure remains diffusion through grain boundaries that form during heat treatments.

One approach to achieve higher recrystallization temperature is to consider ternary compositions. The additional element added to the refractory metal-nitride composition frustrates the recrystallization behavior, rendering a stable amorphous mixture at high temperatures and thus minimizing grain-boundary diffusion. While failure of ternary diffusion barriers still occurs through grain boundaries formed due to decomposition and recrystallization of the film, this process generally takes place at higher processing temperature. For this reason, there is significant interest in ternary nitride alloys, such as Ta–Si–N,7,9 W–Si–N,10,11 W–B–N,12 and Ta–W–N.13

In this study, we report on the diffusion barrier properties of W–Ge–N thin films for Cu metallization. The W–Ge–N alloy is chemically similar to W–Si–N, should be more resistant to recrystallization than WNx, and may prove attractive for integration with SiGe or Ge devices.

The W–Ge–N films were deposited at the rate of 8.64 nm/min on thermally grown SiO2 (630 Å)/n-type (100) Si substrates by reactive sputter deposition. For comparison, WNx films were also deposited under similar conditions. The substrates were sequentially cleaned with trichloroethylene, acetone, and methanol for 5 min each in an ultrasonic bath. The substrates were then loaded into the multitarget rf sputter deposition system via a load lock. The base pressure of the sputtering chamber was 7 × 10–6 Torr. Typical forward sputtering power for the W and Ge targets was 200 W and 100 W, respectively. Nitrogen was incorporated into the films by leaking a mixture of Ar and N2 at the ratio of 1 : 0.9 into the chamber at a fixed chamber pressure of 11.5 mTorr. The thickness of the films was measured using a stylus profilometer. Film thickness was maintained in the range from 300 to 360 nm. All targets were presputtered before deposition to remove contaminants.

To assess the compatibility and diffusion properties of W–Ge–N with respect to Cu metallization, the nitride layer deposition was followed by in situ deposition of a Cu film 90 nm thick. During Cu deposition, Ar gas was used as the sputter deposition gas at a fixed chamber pressure of 15 mTorr. After deposition, the individual samples were an-

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annealed in a separate vacuum chamber with a base pressure of $4 \times 10^{-5}$ Torr at 400, 600, and 800 °C for 1 h to study and compare the diffusion barrier properties of the films. The crystallinity of films and formation of any intermetallic compounds by annealing were characterized by x-ray diffraction (XRD) measurements. Resistivity was measured by the van der Pauw method, while Auger electron spectroscopy (AES) was used to characterize the Cu diffusion profile in the nitride films. Energy dispersive spectrometry was used to determine the composition of the films.

Initial studies focused on the crystallinity of the W–Ge–N films, both as-deposited and after high-temperature annealing. Figure 1 shows XRD spectra of WN<sub>x</sub> and W–Ge–N films, both as-deposited and annealed at 400, 600, and 800 °C. Films of both compositions are amorphous in the as-deposited condition. For the WN<sub>x</sub> films [Fig. 1(a)], recrystallization is clearly evident in the XRD pattern for annealing temperature of 400 °C and higher. The onset of grain structure will provide undesired diffusion paths via the grain boundaries. In contrast, the W–Ge–N film shows no evidence of recrystallization upon annealing at 400 or 600 °C. The XRD data [Fig. 1(b)] for W–Ge–N films annealed at 400 and 600 °C show no peaks related to the nitride material. Only at 800 °C do polycrystalline peaks appear. The addition of Ge to the W–N solid presumably frustrates crystallization, thus rendering the films amorphous for more severe annealing conditions relative to WN<sub>x</sub>. It should also be noted that the W–Ge–N film was far less susceptible to oxidation via ambient atmosphere exposure as compared to WN<sub>x</sub>. This may prove advantageous in terms of device processing.

To assess the behavior of these films as diffusion barriers to Cu, the chemical profile of the annealed structures was determined by Auger electron spectroscopy. Figure 2 shows the depth profiles for the WN<sub>x</sub> film [Fig. 2(a)] as-deposited and upon annealing at [Fig. 2(b)] 600 °C, and [Fig. 2(c)] 800 °C. For the as-deposited diffusion barrier layer in Fig. 2(a), there is a well-defined interface between Cu and WN<sub>x</sub> and the SiO<sub>2</sub> buffer layer is evident. In contrast, after annealing at 600 °C, the Cu signal is seen throughout the barrier layer and into the SiO<sub>2</sub>/Si. This is in agreement with the XRD data, which show the formation of grain structure upon annealing at a temperature of 600 °C. Annealing at 800 °C [Fig. 2(c)] yields a Cu diffusion profile similar to that for the 600 °C anneal. There is also some apparent intermixing of W and SiO<sub>2</sub> seen at the WN<sub>x</sub>/SiO<sub>2</sub> interface in the Auger depth profiles of the annealed samples, which is perhaps related to a change in surface roughness.

The intensity of the nitrogen profile decreases slightly as we increase the annealing temperature to 800 °C. This may reflect the decomposition of WN<sub>x</sub> and liberation of N<sub>2</sub> from the films under those conditions. Affolter et al. have shown that nitrogen is liberated from W–N alloy thin films when annealed at temperatures above 700 °C.

The chemical composition of Cu/W–Ge–N/SiO<sub>2</sub>/Si structures was also examined with AES. Figure 3 shows the chemical depth profiles in[Fig. 3(a)] as-deposited W–Ge–N and after annealing at [Fig. 3(b)] 600 °C and [Fig. 3(c)] 800 °C. In Fig. 3(a), distinct interfaces at the Cu/W–Ge–N and W–Ge–N/SiO<sub>2</sub> boundaries show that there is no Cu diffusion during growth. At an annealing temperature of 600 °C, the interfaces and layers remain distinct, consistent with no or minimal diffusion of Cu through the barrier layer. These results suggest that W–Ge–N films possess superior diffusion barrier properties as compared to WN<sub>x</sub>. At an annealing temperature of 800 °C, Cu is observed in the diffu
position temperature slows nitrogen evolution. Figure 4 robustness of W–Ge–N film, for which increased decompo-

FIG. 3. AES depth profiles of Cu/W–Ge–N/SiO₂/Si (a) as-deposited, (b) annealed at 600 °C/1 h, and (c) annealed at 800 °C/1 h.

tion peaks only at an annealing temperature of 800 °C, sug-
gesting that the addition of Ge frustrates the recrystallization behavior of WNₓ. The AES data show Cu diffusion across the WNₓ layer for an annealing temperature of 600 °C, while for W–Ge–N films the Cu/W–Ge–N and W–Ge–N/SiO₂ interfaces remain distinct at that temperature.. The resistivity of both films decreases with increasing anneal temperature, with the resistivity of WNₓ two orders of magnitude lower than W–Ge–N after annealing. This behavior is consistent with enhanced stability of W–Ge–N with respect to film decomposition and nitrogen evolution.

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FIG. 4. Resistivity vs annealing temperature (a) for W–Ge–N and WNₓ films. Also shown (b) is the resistivity as a function of sputter target power for the Ge and W targets.

In conclusion, the diffusion barrier properties of W–Ge–N thin films have been investigated. XRD shows recrystallization of WNₓ films at an annealing temperature of 400 °C and higher, while W–Ge–N films show recrystallization barrier as seen for the WNₓ film. Again, Cu diffusion correlates with the appearance of grain structure in the film [i.e., (111) reflection of β-W₂N in the XRD pattern]. This is also consistent with N loss suggested by the AES sputter profile, and thus its ability to stuff the diffusion pathways.

The resistivity of the W–Ge–N films was measured using the van der Pauw method. In general, the resistance of the as-deposited W–Ge–N films is higher than WNₓ. As shown in Fig. 4(a), the resistivity of WNₓ and W–Ge–N decreases as the annealing temperature increases. While the resistivity of WNₓ decreases upon annealing at 400 °C, the resistivity for W–Ge–N remains relatively unchanged after annealing at 400 °C. There is a progressive decrease in resistivity for both materials with a further increase in annealing temperature. The change in resistivity correlates with the onset of grain structure, suggesting electron transport across grain boundaries. The decrease may also be due to the loss of nitrogen from the films. The resistivity of WNₓ is two orders of magnitude lower than W–Ge–N at 800 °C reflecting the robustness of W–Ge–N film, for which increased decomposition temperature slows nitrogen evolution. Figure 4(b) shows the resistivity of W–Ge–N films versus sputtering power to the Ge target. Clearly, the resistivity scales with Ge content in the film.