

Properties of Ta–Ge–(O)N as a diffusion barrier for Cu on Si

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The properties of Ta–Ge–(O)N as a diffusion barrier for Cu on silicon have been investigated. Ta–Ge–(O)N was deposited on single crystal *p*-Si(001) by reactive sputtering. This was followed by *in situ* deposition of Cu. Diffusion barrier tests were conducted by subsequent annealing of individual samples in Ar atmosphere at higher temperature. The films were characterized by x-ray diffraction, Auger electron spectroscopy, and four-point probe. The results indicate that Ta–Ge–(O)N fails after annealing at 500 °C for 1 h compared to Ta(O)N which fails after annealing at 400 °C for 1 h indicating better diffusion barrier properties. © 2007 American Institute of Physics. [DOI: 10.1063/1.2435979]

As the minimum feature size in integrated circuits continues to decrease, there is a need to replace Al in interconnects due to the limited conductivity and poor electromigration performance of Al under high current densities. Cu is a viable alternative for replacing Al due to its 1.7 times lower resistivity compared to Al and better electromigration properties under high current densities.^{1,2} In addition, the *RC* time delay achieved by an Al/SiO₂ stack needs to be lowered significantly to increase the device speed. The *RC* time constant can be significantly lowered by combining Cu with a low-*k* material, thus enhancing the performance of the device.³

Although the aforementioned properties of Cu are advantageous for device manufacture, Cu diffuses very effectively through Si, SiO₂, and Ge, degrading the electrical properties of the device.⁴ It is an acceptor in Ge introducing traps at $E_v + 0.04$ eV, $E_v + 0.32$ eV, and $E_c - 0.26$ eV.⁵ Cu is a donor in Si and creates traps from 0.2 to 0.5 eV above the valence band.⁶ It also reacts with Si to form parasitic copper silicides at the interface. In addition, Cu reacts with dopants in Si to form complexes that affect the device characteristics.⁷ Thus, the use of Cu as an interconnect for future technology nodes will require a viable diffusion barrier. There has been a significant interest in refractory nitrides such as WN_{*x*}, TiN, HfN_{*x*}, and TaN (Refs. 8–16) as diffusion barrier candidates for Cu metallization. These diffusion barriers, however, typically fail at moderate temperature (400–600 °C) limiting their use. The primary mode of failure for these diffusion barriers is by Cu diffusion through grain boundaries formed by recrystallization of the barrier material upon annealing. By increasing the recrystallization temperature, grain boundary formation can be delayed, thereby increasing the robustness of the diffusion barrier. Addition of a third element to the binary matrix induces amorphization at room temperature and also delays the recrystallization process, making ternary solutions interesting as diffusion barrier candidates. Some of the ternary nitride dif-

fusion barriers being studied include W–Si–N, Ta–Si–N, and W–Ge–N.^{17–19}

In this letter, we report on the barrier layer properties when Ge is added to Ta(O)N. Ge is of interest because it displays chemical behavior similar to that of its congener Si and might be compatible with future Ge and SiGe based devices. Diffusion barrier properties of Ta–Ge–(O)N were compared with Ta(O)N deposited under identical conditions. The results indicate that a Ta–Ge–(O)N diffusion barrier fails at a higher temperature than Ta(O)N, suggesting superior diffusion barrier properties.

Ta–Ge–(O)N diffusion barriers were deposited on *p*-Si(001) wafers by reactive sputtering process at room temperature. Prior to deposition, the wafer was etched in 7:1 buffered oxide etch to remove its native oxide and then rinsed with de-ionized water. The substrate was loaded in the sputtering chamber that is maintained at 3×10^{-7} Torr base pressure. Sputtering targets were presputtered before deposition at an Ar pressure of 15 mTorr to remove any contamination on the surface. The forward powers used for Ta and Ge were 200 and 100 W, respectively. The diffusion barrier films were then deposited by flowing Ar and N₂ at a chamber pressure of 10 mTorr. For comparison, Ta(O)N diffusion barriers were deposited under identical circumstances. The diffusion barrier film thickness was maintained at 50 nm in all cases.

Cu was then deposited on the nitride *in situ* at room temperature without breaking the vacuum. Presputtering of the Cu target was carried out to remove any contaminants prior to deposition. The forward sputtering power for Cu was 200 W. Cu was deposited on the diffusion barrier by flowing ultrahigh purity Ar gas at a chamber pressure of 5 mTorr. The thickness of Cu was maintained at 300 nm in all cases. Substrates were rotated at 20 rpm during all depositions to maintain film uniformity. Individual samples were then annealed separately in a tube furnace in the temperature range of 400–700 °C for 1 h. Before annealing, the furnace tube was purged by flowing Ar gas at 65 SCCM (SCCM denotes cubic centimeter per minute at STP) for at least 10 h. The diffusion barrier analysis was conducted using a Phillips

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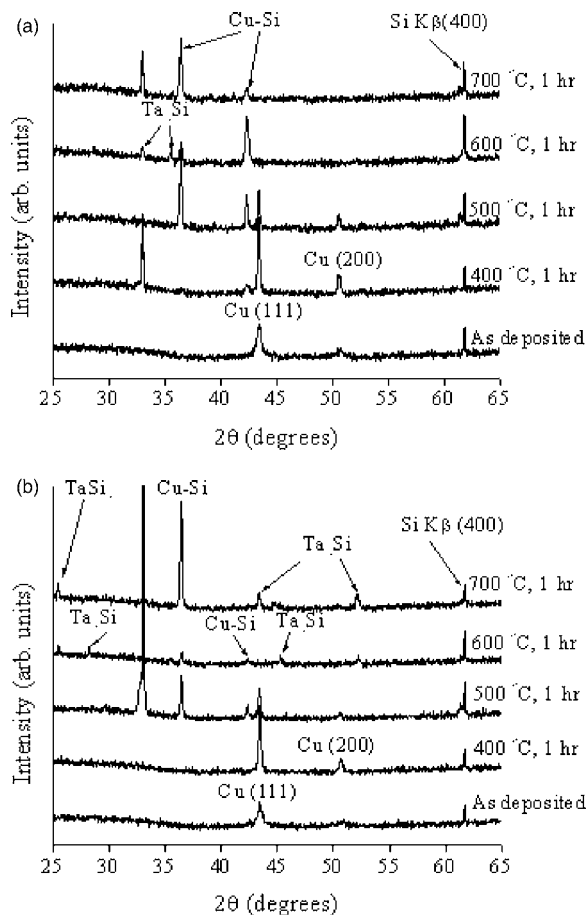


FIG. 1. X-ray diffraction patterns of as deposited and annealed at the temperature shown in figure of (a) Cu/Ta(O)N/Si (001) for 1 h and (b) Cu/Ta-Ge-(O)N/Si (001) for 1 h.

APD 3720 x-ray diffractometer (XRD) to detect any intermetallic phase formation between Cu and Si, which would indicate bulk Cu diffusion in the substrate leading to barrier failure. The chemical depth profile of Cu through the diffusion barrier was determined by Auger electron spectroscopy (AES) Perkin-Elmer PHI 660 scanning Auger multiprobe. Sheet resistance of Cu was measured by four-point probe.

Figure 1 shows the x-ray diffraction patterns for Cu/Ta(O)N/Si and Cu/Ta-Ge-(O)N/Si both as deposited and after annealing in the temperature range of 400–700 °C for 1 h. As evident from Fig. 1, both Ta(O)N and Ta-Ge-(O)N films are amorphous in as-deposited condition with only Cu (111) and (200) peaks present. Upon annealing at 400 °C in Ar atmosphere for 1 h, sufficient Cu diffuses through Ta(O)N into the Si substrate to form copper silicide [Fig. 1(a)], indicating diffusion barrier failure. This could be due to recrystallization of Ta(O)N and formation of nanocrystalline grains. Cu film crystallinity increases after 400 °C annealing, as evidenced by the sharpening of the Cu (111) and (200) peaks. Further annealing at higher temperature induces bulk Cu diffusion into the Si substrate as evidenced by a decrease in the intensity of the Cu peaks after 500 °C annealing. After 600 °C, the Cu peak finally disappears with a corresponding increase in copper silicide peak intensity, indicating complete Cu diffusion through the Ta(O)N diffusion barrier. In comparison, for the Ta-Ge-(O)N diffusion barrier there is no formation of copper silicide peaks after annealing at 400 °C, indicating superior diffusion barrier properties [Fig. 1(b)]. Cu film crystallinity

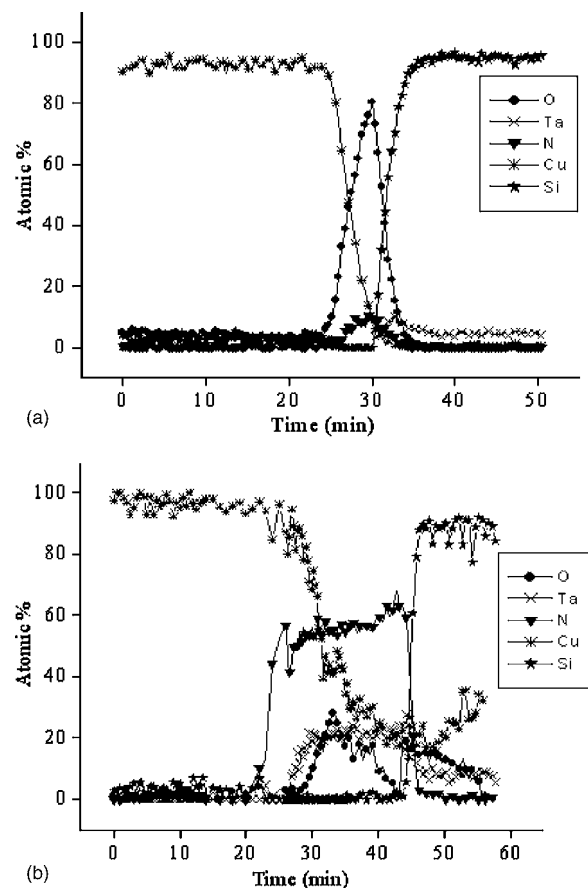


FIG. 2. AES depth profile of Cu/Ta(O)N/Si (001) for (a) as deposited and (b) annealed at 400 °C for 1 h.

increases as evident by an increase in sharpness of Cu (111) and (200) peaks. Only after annealing the Ta-Ge-(O)N diffusion barrier films at 500 °C does the observation of copper silicide peaks indicates barrier failure. Subsequent annealing at higher temperature results in behavior similar to that of Ta(O)N. The addition of Ge to the binary Ta(O)N matrix, however, raises the diffusion barrier failure temperature by at least 100 °C, resulting in better diffusion barrier properties of Ta-Ge-(O)N films.

The chemical depth profile of Cu through the diffusion barrier was determined by Auger electron spectroscopy. Figure 2 shows the Auger depth profile for Cu/Ta(O)N/Si as-deposited and after annealing at 400 °C for 1 h. The as-deposited depth profile shows distinct interfaces at Cu-Ta(O)N and Ta(O)N-Si layers indicating no Cu diffusion. The high oxygen content in the film is due to possible leak in the nitrogen line and background oxygen in the deposition chamber. After annealing at 400 °C, however, Cu signal is seen throughout the diffusion barrier and into the substrate suggesting significant Cu diffusion and thus Ta(O)N barrier failure. This supports the XRD data in which copper silicide peak formation is evident after 400 °C annealing [Fig. 1(a)]. Figure 3 shows the Auger depth profile for the Cu/Ta-Ge(O)N/Si structure as deposited and after annealing at 400 °C for 1 h. In contrast to Ta(O)N, the Cu/Ta-Ge(O)N and Ta-Ge-(O)N/Si interfaces are quite distinct both in as-deposited condition and after annealing at 400 °C for 1 h. The Cu profile is almost identical for Figs. 3(a) and 3(b), indicating no Cu diffusion through the diffusion barrier. The thickness of Cu film in annealed sample

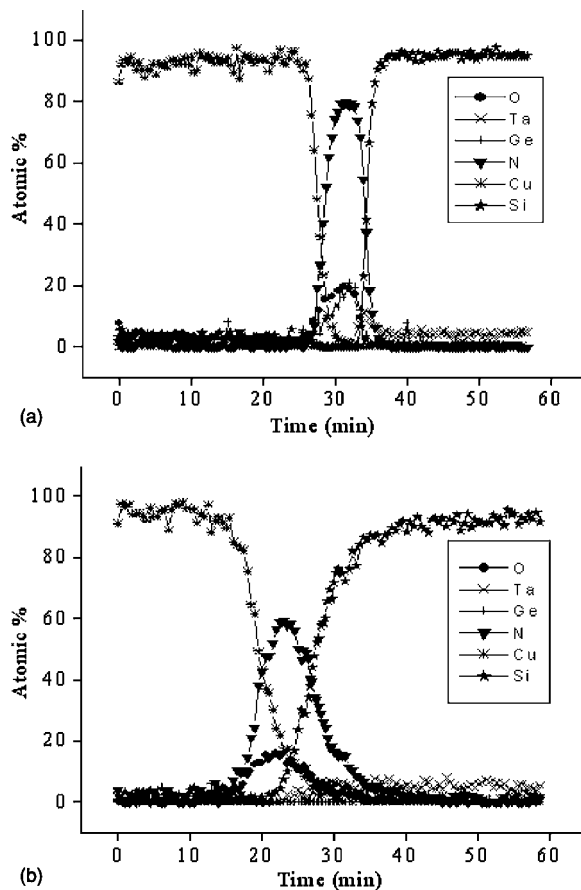


FIG. 3. AES depth profile of Cu/Ta-Ge-(O)N/Si (001) for (a) as-deposited and (b) annealed at 400 °C for 1 h.

[Fig. 3(b)] is less as compared to as-deposited Ta-Ge-(O)N films [Fig. 3(a)]. This could be due to the small amount of copper diffusion in the barrier and subsequent reaction with germanium. The lack of evidence for copper diffusion in the depth profile is consistent with the XRD data that show no copper silicide peak formation even after annealing at 400 °C.

Cu sheet resistance was measured by four-point probe. Figure 4 shows the sheet resistance of Cu for Ta(O)N and

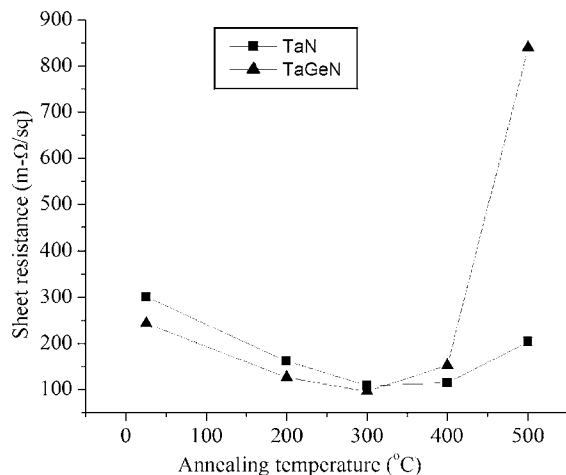


FIG. 4. Sheet resistance of Cu vs annealing temperature for Ta(O)N and Ta-Ge-(O)N.

Ta-Ge-(O)N in as-deposited and after high temperature annealing conditions. The sheet resistance of Cu decreases after annealing until 300 °C or higher for both Ta(O)N and Ta-Ge-(O)N. This could be due to grain growth and increased crystallization of Cu after annealing. Increase in grain size causes decrease in grain boundaries, which contributes to lower electron scattering. Upon annealing at 500 °C (Fig. 4), the sheet resistance of Cu increases drastically. This increase is consistent with Cu diffusion and formation of copper silicides as evident by x-ray diffraction patterns.

In summary, the properties of Ta-Ge-(O)N thin films as diffusion barriers for Cu have been investigated. X-ray diffraction patterns showed that the addition of Ge to the binary Ta(O)N matrix causes the diffusion barrier failure temperature to increase by at least 100 °C as compared to Ta(O)N. The AES depth profile showed significant Cu diffusion through Ta(O)N diffusion barriers and into the Si substrate after annealing at 400 °C, while no Cu diffusion occurs at similar temperature through the Ta-Ge-(O)N diffusion barrier suggesting superior diffusion barrier properties of Ta-Ge-(O)N thin films. The sheet resistance of Cu initially decreased with increase in annealing temperature for both Ta(O)N and Ta-Ge-(O)N suggesting Cu grain growth. With further temperature increase, Cu diffusion eventually occurs through both diffusion barriers leading to formation of highly resistive copper silicides with a corresponding increase in the Cu sheet resistance.

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