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Encapsulation of Ag films on SiO_2 by Ti reactions using Ag–Ti alloy/bilayer structures and an NH_3 ambient

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Thin encapsulated silver films have been prepared on oxidized silicon by nitridation of ~200-nm-thick Ag–19 at. % Ti alloy films and Ag(120 nm)/Ti(22 nm) at 300–700 °C in an ammonia ambient. The encapsulation process has been studied in detail by Rutherford backscattering, and scanning Auger and secondary-ion-mass spectrometry, which showed that Ti-nitride and Ti-oxide-silicide formation take place at the surface and the Ag–Ti/SiO_2 interface, respectively. Four-point-probe analysis of the alloy films suggests that the resistivity is controlled by the residual Ti concentration. Resistivity values of ~4 $\mu\Omega$ cm were measured in encapsulated Ag alloy films with initial low Ti concentrations. The annealed bilayer structure had minimal Ti accumulations in Ag and the resistivity values were comparable to that of the as-deposited Ag (~3 $\mu\Omega$ cm). © *1996 American Institute of Physics.* [S0003-6951(96)03923-X]

The electrical connections in integrated circuits (IC) are provided by a metallization scheme, which in the case of very-large-scale integration (VLSI) is based on Al-alloy line structures. As IC technologies move toward ultralarge-scale integration (ULSI), Cu- and Ag-based metallization schemes are being considered for replacing the conventional Al-based schemes.[1] Elemental Cu and Ag have low resistivities and better electromigration resistance than Al. Such improved inherent properties have become required specifications for metallization with feature sizes less than 0.25 μm.

Metallization line structures are required to have structural integrity and good electrical conductivity, and they must maintain these properties throughout subsequent fabrication and operation of the IC. One concern regarding structural integrity is the poor adhesion of Cu and Ag to dielectric materials, such as SiO_2. Another potential concern is Ag agglomeration, which has been observed when annealing takes place in air.[2] Tarnishing of Ag in sulfur environments,[3] and the oxidation of Cu will require passivation layers to ensure structural integrity.[4] Reinforcing the structural integrity can be accomplished by interfacial chemical reactions. Such reactions should limit themselves to the formation of thin reaction layers that promote adhesion and prevent atomic transport between the metal and its surroundings (i.e., provide thin diffusion barriers). In cases where adjoining materials do not display this behavior, a desired interfacial structure can often be formed by adding appropriate elemental films or alloying elements to the metal. This approach has been taken in studies of Al, Mg, Ti, and Cr additions in connection with Cu metallization.[5–7]

Simultaneous preparation of both sides of a Cu film has been accomplished by exposing the Cu–Ti bilayer or alloy surface to an NH_3 ambient.[6,7] At reaction temperatures between 350 and 600 °C, Ti nitride, TiN(O), is formed on the top surface, whereas, a Ti silicide–oxide bilayer is formed between the Cu and SiO_2. The presence of oxygen in TiN(O) is due to residual oxygen in the NH_3 ambient.[6,7] This letter reports on such an ''encapsulation'' process for Ag, where the Ti is introduced by deposition of Ag–Ti alloys and bilayers. This approach has demonstrated more promise in obtaining low-resistivity films than encapsulation of Cu.

The Ag–Ti depositions were prepared on Si wafers with 210-nm-thick thermally grown oxides. The alloy structures consisting of ~200-nm-thick Ag–x% Ti (where $x=6$, 10, 18, 19, and 26 at. %) films were made by dual electron-beam deposition. The bilayer structure corresponded to 15 at. % Ti, and were prepared by sputter deposition of a 22-nm-thick Ti film followed by 120 nm Ag without breaking vacuum. The encapsulation process took place at 300–700 °C in a fused-quartz-tube furnace using a flowing NH_3 ambient of 99.99% purity and a flow rate of 2 l/min at atmospheric pressure. The encapsulated Ag films have been characterized by depth profiling: Rutherford backscattering spectrometry (RBS), Auger electron spectroscopy (AES), and secondary-ion-mass spectrometry (SIMS). Glancing-angle x-ray-diffraction and four-point-probe resistance measurements were used to determine the films' structural and electrical properties.

The encapsulation of Ag proceeded in a similar way to that of Cu. After annealing in an NH_3 ambient for 30 min, the surface changed to have a golden color indicative of TiN formation. The results of the RBS characterization are shown in Fig. 1 and 2. Only the Ti and Ag backscattered signals are displayed, and the Ti signal in Fig. 1 shows clearly that the 500 °C anneal causes Ti to segregate at the surface (see peak labeled ''Ti surface''). The RBS spectra in Fig. 2, where the actual Ti signal has been enhanced by a factor of 3, show that Ti in the alloy segregates to the surface and interface upon annealing. AES and SIMS profiling show evidence for TiN(O) formation at the surface and Ti-oxide-silicide bilayer formation at the interface. Based on the RBS, the surface layers on the alloy correspond to 17 (450 °C anneal) and 23

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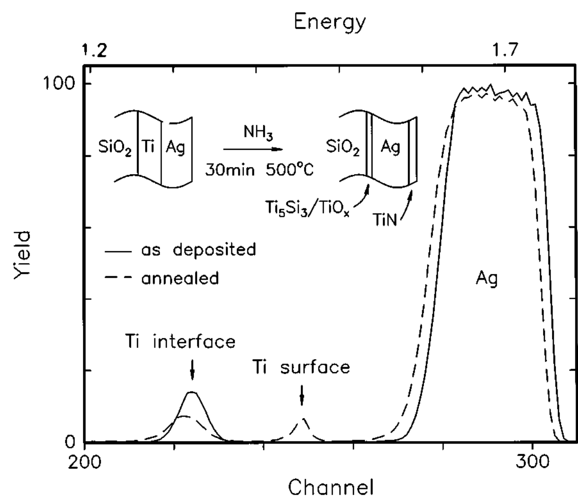

FIG. 1. Ag encapsulation on SiO_2 prepared from Ag(120 nm)/Ti(22 nm) bilayers. RBS spectra show the depth distributions of Ag and Ti before and after annealing at 500 °C in an ammonia ambient for 30 min. The spectra were obtained using a 2.0 MeV He^{++} beam and a scattering angle of 170 °.

(600 °C anneal) nm-thick TiN films (Fig. 2), respectively, whereas the surface layer on the bilayer corresponds to 10 nm TiN (Fig. 1). The interfacial bilayer is expected to consist of TiO_w ($w \sim 1.1$) and Ti_5Si_3, the reaction products from the Ti–SiO_2 reaction.[7]

The Ti signal in Fig. 2 shows that, as the reactions consume Ti, the Ag film becomes gradually dealloyed. The Ti solubility in Ag is 2.0 at. % at 600 °C,[8] and the dealloying process appears to take place by Ti out-diffusion (presumably grain-boundary diffusion in Ag with a diffusion coefficient, which is estimated to be larger than 10^{-12} cm^2/s). The diffusion is primarily driven by chemical forces arising from the enthalpy difference between reacted Ti (compounds formed with N, O, and Si) and alloyed Ti. Residual Ti concentration levels of 8.0% and 1.5% were measured in the alloy by RBS after 450 and 600 °C, respectively. In the case

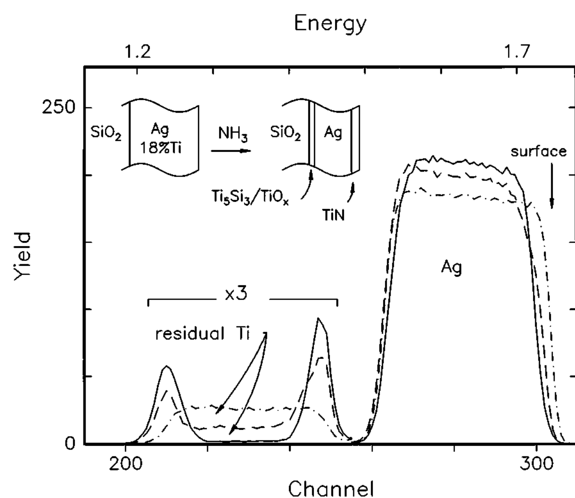

FIG. 2. Ag encapsulation on SiO_2 prepared from 210-nm-thick Ag–18 at. % Ti alloy films. RBS spectra show the depth distributions of Ag and Ti before (· - · -) and after annealing at 450 (- -) and 600 °C (—) in an ammonia ambient for 30 min. The Ti signal has been multiplied by a factor of 3.

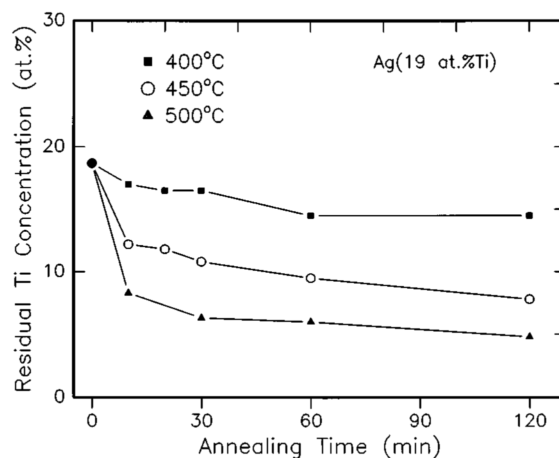

FIG. 3. Dealloying kinetics obtained with Ag–19% Ti alloy films. The residual Ti concentration is shown as a function of annealing time for three different temperatures. The annealing took place in an ammonia ambient and the data were obtained using 2.0 MeV He^{++} RBS.

of bilayers, less than 1 at. % Ti has accumulated in the Ag film after encapsulation.

The Ti depth distribution in Fig. 2 shows separation between reacted and alloyed Ti resulting in three regions: TiN(O) surface layer, residual Ti in the Ag alloy, and an interfacial Ti-oxide-silicide bilayer. It is observed that the segregation of Ti and the corresponding dealloying increases with temperature. The time dependence of the encapsulation process was also studied by RBS analysis. Figure 3 shows the residual Ti concentration in the Ag–19 at. % Ti alloy as a function of annealing time for three annealing temperatures. The results obtained are characterized by rapid dealloying/segregation followed by a plateau in the dealloying rate. A similar kinetic behavior was obtained with a Ag–26% Ti film. Compared with the data in Fig. 3, the dealloying of the high-Ti concentration alloy gave more flat curves and the residual Ti concentrations were higher.

The resistivity of the Ag films was measured by four-point-probe measurements, and the result of this study is presented in Tables I and II. Table I lists the measured resistivities of the alloys after annealing, and they are seen to be controlled by the residual Ti concentration. A strong temperature dependence is apparent but is primarily caused by the residual Ti concentration. Resistivity values of <5 $\mu\Omega$ cm are strong evidence that the pure elemental phase and not an intermetallic phase (TiAg or Ti_2Ag)[8] is the dominant film component. Phase identification was done by glancing-

TABLE I. Room-temperature resistivity of encapsulated Ag films prepared from 210-nm-thick Ag–18% Ti. The resistivity was obtained from four-point-probe and RBS thickness measurements. Also shown are the corresponding Ag alloy compositions and annealing temperatures.

Annealing temperature (°C)	Ti concentration (at. %)	Resistivity ($\mu\Omega$ cm)
As deposited	17.6	140.
350	17.0	69.6
450	8.0	15.0
500	5.0	9.2
600	1.5	4.8

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TABLE II. Room-temperature resistivity of encapsulated Ag films prepared from Ag(120 nm)/Ti(22 nm) bilayers. The resistivity was obtained from four-point-probe and RBS thickness measurements. The Ti concentration were in all cases below the RBS detection limit, i.e., (<1 at. % Ti).

Annealing temperature (°C)	Resistivity ($\mu\Omega$ cm)
As deposited	3.1
450	3.5
500	3.4
600	3.2

angle x-ray diffraction (results not shown), only the Ag(111), Ag(200), and Ag(222) signals were observed in both the annealed and unannealed samples.

ULSI applications will require that the encapsulated Ag films have a low resistivities, comparable to the elemental resistivity of Al(2.74 $\mu\Omega$ cm) and approaching those of Cu (1.70 $\mu\Omega$ cm) and Ag (1.61 $\mu\Omega$ cm).[9] The resistivity's dependence on the Ti concentration as seen in Table I is weaker than expected from dilute substitutional-alloy theory.[10] Nevertheless, substantial dealloying of Ti from Ag to levels below 1 at.% is necessary to obtain resistivities below 3 $\mu\Omega$ cm. The resistivity contribution from the Ti impurities is primarily a problem of the alloys, since the bilayers did not show Ti accumulations exceeding the detection limit of ~1 at. %. The 3 $\mu\Omega$ cm resistivity level in the case of bilayers (see Table II) is instead controlled by the limitation of the deposition process. However, sputter-deposited Ag films have been prepared, which have near-bulk resistivity.[11]

This resistivity study suggests that highly conductive Ag films can be prepared from alloys by optimizing the process variables associated with the film deposition and the encapsulation process. Results in the literature suggest that the proposed encapsulation process prevents diffusion[7] and promotes adhesion[6] as well as electromigration resistance.[2] These properties will be addressed in future studies as well as the evolution of microstructure responsible for the dealloying kinetics.

In conclusion, thin encapsulated Ag films were prepared on oxidized silicon. The encapsulation was formed by Ti reactions using both Ag–Ti alloy films and Ag–Ti bilayer structures in an NH_3 ambient. Ti segregation was observed at the surface and interface. Evidence was presented for TiN(O) formation at the surface and Ti oxide silicide at the interface. The resistivity of the Ag film appears to be controlled by the Ti concentration. Resistivity values of ~4 $\mu\Omega$ cm were measured in encapsulated Ag alloy films which were alloyed with low initial Ti concentrations. Nitridation of the bilayer resulted in minimal Ti accumulation in Ag, and the resistivity was comparable to that of the as-deposited Ag (~3 $\mu\Omega$ cm). Kinetic studies showed that the encapsulation reaction takes place within the first 10 min. This happened for all annealing temperatures; the amount of dealloying increased with temperature. Lower residual Ti levels were observed with lower initial Ti concentration. Alloys prepared with lower Ti concentrations are therefore expected to result in low-resistivity encapsulated Ag films.

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