Low temperature plasma-promoted chemical vapor deposition of tantalum from tantalum pentabromide for copper metallization

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A low temperature plasma-promoted chemical vapor deposition (PPCVD) process has been developed for the growth of tantalum (Ta) from the halide source tantalum pentabromide (TaBr_5), using hydrogen as reducing agent, for incorporation in emerging integrated circuitry (IC) copper metallization schemes. Ta films were produced at substrate temperatures of 400–450 °C, reactor working pressures of 0.6–0.7 Torr, hydrogen carrier flow rate of 50 sccm, hydrogen reactant flow rates between 200 and 1200 sccm, and plasma power ranging from 20 to 100 W, corresponding to a power density of 0.11–0.55 W/cm². The films were subsequently characterized by Auger electron spectroscopy (AES), Rutherford backscattering (RBS), x-ray diffraction (XRD), atomic force microscopy (AFM), four-point resistivity probe, scanning electron microscopy (SEM), and cross-section SEM. These studies indicated that the Ta films thus produced were carbon and oxygen free, contained bromine concentration below 2.5 at. %, and exhibited better than 75% step coverage in nominally 0.6 μm , 2.5:1 aspect ratio, trench structures. © 1998 American Vacuum Society. [S0734-211X(98)01305-5]

Current microelectronics technologies require diffusion barrier/adhesion promoter layers in the various levels of intrachip metallization schemes to prevent undesirable diffusion and interactions of conductor plugs and interconnects with surrounding dielectrics, which could lead to reliability problems and device failure. These barrier layers must also be able to withstand repeated thermal processing, and serve as strong adhesion promoters to ensure structural integrity of the signal-carrying metallization stacks.¹

Various material systems, such as refractory metals, their nitrides, and ternary metal–silicon–nitrogen compounds, have been investigated for such applications.² In the case of copper-based metallization schemes, tantalum (Ta) is considered among the most suitable candidates. Ta is a highly refractory metal which is stable to an extremely high temperature (melting point=2996 °C).³ It is also known to be thermodynamically stable with respect to Cu because of the absence of Cu–Ta compounds. For instance, a sputtered Ta thin barrier with 50 nm thickness has demonstrated its resistance to Cu diffusion up to 550 °C for 1 h.⁴

Tantalum growth can be achieved by many techniques. However, chemical vapor deposition (CVD) offers several advantages over traditional “line-of-sight” physical vapor deposition (PVD) techniques. Among these are improved step coverage and higher growth rates. Alternatively, emerg-

ing PVD technologies, such as collimated and ionized sputtering, might be difficult to integrate with key low dielectric constant materials, in view of the structural and chemical damage that could be induced by the heavy Ta ions into the fragile dielectric matrix. In this respect, the availability of low temperature CVD processing represents a viable route to the integration of Ta liners with thermally sensitive dielectric materials.

Earlier attempts at CVD Ta employed mostly TaCl_5 as precursor.⁵ Unfortunately, the processing temperature required to produce Ta films were in excess of 900 °C, and thus seriously limited its usefulness. The strategy espoused herein has focused, instead, on low temperature plasma-promoted CVD (PPCVD) of Ta from tantalum pentabromide (TaBr_5) with hydrogen as a reducing agent. The choice of tantalum pentabromide (TaBr_5), which belongs to the same class of halide chemistries as TaCl_5 , as source precursor was mandated primarily by energetic considerations. Primarily, its heat of formation is –143 kcal/mol, as compared to –205 kcal/mol for TaCl_5 ,⁶ implying that TaBr_5 could potentially decompose at significantly lower temperature than TaCl_5 . Further reduction in processing temperature could be achieved by employing a low power hydrogen plasma, given the critical role that atomic or ionic hydrogen plays in the TaBr_5 reduction process

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FIG. 1. XRD results of PPCVD proceeded Ta films.

The use of TaBr_5 is supported by the expectation that the activation energy for bromine diffusion might be higher than chlorine, given that Br is appreciably heavier than Cl. This expectation is supported by investigations of the fluorine and chlorine interaction with silicon (111).⁷ Resulting findings showed that the barrier for chlorine penetration into silicon is much larger than that for fluorine. This behavior was attributed to the larger size, and hence higher ionicity and resulting Coulomb interaction, of chlorine versus fluorine. It is also supported by *ab initio* Hartree-Fock studies of the nature of the bonding between the three halogens F, Cl, and Br and silver Ag(111) surface, which indicated that the interaction of these halogens with the metal surface is dominantly ionic.⁸ Similar findings were reported for the diffusion characteristics of iodine and chlorine from TiN films formed by thermal CVD (TCVD) from the halide precursors tetraiodotitanium (TiI_4) and tetrachlorotitanium (TiCl_4).⁹

These investigations have important implications for the effects of residual bromine concentrations in tantalum-based films, and imply that higher thermal energy might be needed

FIG. 2. (a) AFM top view micrograph of a PPCVD grown Ta film; (b) AFM surface plot of a PPCVD grown Ta film.

FIG. 3. Typical AES depth profile of a PPCVD grown Ta film.

for Br versus Cl to diffuse out of the Ta lattice. In this letter, results are reported from a study of development and optimization of a low temperature ($\leq 450^\circ\text{C}$) PPCVD process for the growth of Ta from TaBr_5 for incorporation in emerging copper-based interconnect technologies and beyond.

Process development was performed in a custom-designed 5 in. wafer, warm wall, plasma capable, stainless steel CVD reactor. A standard pressure-based delivery unit was applied for the delivery of the solid TaBr_5 precursor. A stainless-steel parallel-plate configuration was employed for the radio-frequency plasma (13.56 MHz) generation, with the substrate placed on the heated bottom (ground) electrode. Electronic mass-flow controllers were used to measure the flow rates of carrier and reactant gases, and process pressures were measured with baratron gauges. A cryopump was employed to ensure reactor cleanliness prior to deposition runs, with base pressures typically in the 10^{-6} Torr range. Alternatively, a mechanical pump was used during actual processing. A load lock was used to prevent atmospheric contamination of the deposition chamber during wafer loading. Before deposition began, a soft hydrogen plasma predeposition clean was performed on substrate. Then the substrate was heated to the desired deposition temperature, and film growth was initiated as the precursor sublimator was heated to a preset temperature ($120\text{--}180^\circ\text{C}$). Ta films were deposited at substrate temperatures of $400\text{--}450^\circ\text{C}$, reactor working pressures of 0.6–0.7 Torr, hydrogen carrier flow rate of 50 sccm, hydrogen reactant flow rates of 200–1200 sccm, and plasma power of 20–100 W (with an equivalent power density of $0.11\text{--}0.55\text{ W/cm}^2$).

The PPCVD produced Ta films were metallic, continuous, and mirror bright. X-ray diffraction (XRD) analyses of the PPCVD-produced Ta films, as shown in Fig. 1 for a 700-Å-thick film on Si, indicated a polycrystalline Ta β phase with major diffraction peaks appearing at $2\theta = 33.67^\circ$ (002), 36.33° (410), 39.16° (212), 40.12° (411), 64.71° (413). In addition, the diffraction peaks were broad and overlapping, implying small Ta grain size.

This XRD result is supported by AFM findings. AFM was performed using a Nanoscope III multimode atomic force microscope. Data were collected in tapping mode AFM with silicon cantilevers at resonance frequencies in the range of 200–300 kHz. The AFM top view micrograph, as displayed

FIG. 4. RBS spectrum of a PPCVD produced Ta film.

in Fig. 2(a) for a 700-Å-thick PPCVD grown Ta film, indicated that the surface morphology of the Ta films consisted of small grains with mean grain size of $\sim 8\text{ nm}$. The Ta films also exhibited smooth surface morphology with root-mean-square (rms) surface roughness of $\sim 1.8\text{ nm}$, as shown in AFM surface plot of Fig. 2(b).

The composition of the films was determined by Auger electron spectroscopy (AES) and Rutherford backscattering (RBS) techniques. AES was performed using a physical electronics Model 15-110B cylindrical mirror analyzer (CMA). A primary electron energy of 5 keV at 1 mA was employed, and the results were standardized using a 99.98% Ta foil standard. Figure 3 exhibits typical AES depth profile of a PPCVD grown Ta film. It indicated that within the detection limits of AES, the films were made of a pure Ta phase. No oxygen, carbon, or nitrogen were detected in the films.

RBS spectra were taken using a 2 MeV He^+ beam, and calibrated with bulk samples of gold and carbon. The RBS results, shown in Fig. 4 for a 400-Å-thick Ta film on Si, confirmed the AES findings that the PPCVD process yielded Ta films with less than 2.5 at. % bromine. Four point probe resistivity measurement yielded film resistivity of about $120\ \mu\Omega\text{ cm}$, which is consistent with the reported resistivity of

FIG. 5. Typical CS-SEM micrograph of a PPCVD grown Ta film.

sputtered β -phase Ta films (110–300 $\mu\Omega$ cm).¹⁰ Associated kinetic studies indicated that Ta growth rates ranged between 15 and 80 Å/min, depending on process parameters.

Scanning electron microscopy (SEM) and cross-section SEM (CS-SEM) analyses were carried out on a Zeiss DSM 940 microscope, employing a 20 keV primary electron beam. SEM and CS-SEM results showed the deposited films to be quite dense with no columnar grain growth. Cross-section SEM studies of film conformality on patterned test wafers, as shown in Fig. 5, indicated that PPCVD could achieve better than 75% step coverage in nominally 0.6 μ m, 2.5:1 aspect ratio, trench structures.

In summary, a low temperature (≤ 450 °C) PPCVD process has been developed for the growth of Ta from TaBr₅ with H₂ as reducing agent. The analysis results showed that PPCVD produced, β phase, Ta films were C, O, and N free, contained bromine concentration below 2.5 at. %, and exhibited good step coverage. These studies indicated that low temperature PPCVD of Ta from TaBr₅ might provide a viable route for diffusion barrier applications in emerging copper metallization schemes. More investigations are presently under way to further refine and optimize the CVD process,

and fully characterize the resulting materials in terms of composition, texture, electric characteristics, and diffusion barrier performance.

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¹G. P. Rao, *Multilevel Interconnect Technology* (McGraw-Hill, New York, 1994).

²M. Takeyama, A. Noya, T. Sase, and A. Ohta, *J. Vac. Sci. Technol. B* **14**, 674 (1996).

³*CRC Handbook of Chemistry and Physics*, 71th ed., edited by D. Lide (CRC, Boston, 1990), pp. 4–109.

⁴J. S. Reid, E. Kolawa, and M. Nicolet, *J. Mater. Res.* **7**, 2424 (1992).

⁵K. Hieber, *Thin Solid Films* **24**, 157 (1974).

⁶I. Barin, O. Knacke, and O. Kubaschewski, *Thermochemical Properties of Inorganic Substances* (Springer, Berlin, 1977).

⁷M. Seel and P. S. Bagus, *Phys. Rev. B* **28**, 2023 (1983).

⁸P. S. Bagus, G. Pacchioni, and M. R. Philpott, *J. Chem. Phys.* **90**, 4287 (1989).

⁹C. Faltermeier, C. Goldberg, M. Jones, A. Upham, D. Manger, G. Peterson, J. Lau, and A. E. Kaloyeros, *J. Electrochem. Soc.* **144**, 1002 (1997).

¹⁰P. N. Baker, *Thin Solid Films* **14**, 3 (1972).