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Thermal ALD of Cu via Reduction of Cu_xO films for the Advanced Metallization in Spintronic and ULSI Interconnect Systems

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Abstract—In this work, an approach for copper atomic layer deposition (ALD) via reduction of Cu_xO films was investigated regarding applications in ULSI interconnects, like Cu seed layers directly grown on diffusion barriers (*e. g.* TaN) or possible liner materials (*e. g.* Ru or Ni) as well as non-ferromagnetic spacer layers between ferromagnetic films in GMR sensor elements, like Ni or Co. The thermal Cu_xO ALD process is based on the Cu (I) β -diketonate precursor [$(\text{Bu}_3\text{P})_2\text{Cu}(\text{acac})$] and a mixture of water vapor and oxygen (“wet O_2 ”) as co-reactant at temperatures between 100 and 130 °C. Highly efficient conversions of the Cu_xO to metallic Cu films are realized by a vapor phase treatment with formic acid (HCOOH), especially on Ru substrates. Electrochemical deposition (ECD) experiments on Cu ALD seed / Ru liner stacks in typical interconnect patterns are showing nearly perfectly filling behavior. For improving the HCOOH reduction on arbitrary substrates, a catalytic amount of Ru was successful introduced into the Cu_xO films during the ALD with a precursor mixture of the Cu (I) β -diketonate and an organometallic Ru precursor. Furthermore, molecular and atomic hydrogen were studied as promising alternative reducing agents.

Keywords: Atomic Layer Deposition (ALD), Copper Oxide, Ruthenium, Formic Acid, Hydrogen, Reduction, ULSI Interconnect, Electrochemical deposition (ECD), Spintronic

I. INTRODUCTION

Copper as a functional material plays an essential role in electronic applications. Multi-level metallization systems in today's copper-based ultralarge-scale integrated electronic circuits (ULSI) require the fabrication of diffusion barriers and conductive seed layers for the electrochemical metal deposition (ECD). Such films of only several nanometers in thickness have to be deposited void-free and conformal in patterned dielectrics. The envisaged further reduction of the geometric dimensions of the interconnect system calls for coating techniques that circumvent the drawbacks of the well-

established physical vapor deposition [1]. The atomic layer deposition method (ALD) allows depositing films on the nanometer scale conformally both on three-dimensional objects as well as on large-area substrates. Another prominent utilization of copper is its application as non-magnetic conductive spacer layer between ferromagnetic layers (*e. g.* Co or Ni) in giant magnetoresistance (GMR) sensor elements. The spin-dependent scattering in magnetic films is exploited in read heads for hard drives, random access memories, and galvanic isolators [2]. The use of ALD could be appropriate to obtain atomic layer controlled film stacks with sharp interfaces, which is necessary for large GMR effects [3].

II. EXPERIMENTAL

In this work, metallic copper films are formed via gas phase reduction of copper oxide layers prepared by thermal ALD. The ALD process is based on the Cu (I) β -diketonate precursor [$(\text{Bu}_3\text{P})_2\text{Cu}(\text{acac})$] and a mixture of water vapor and oxygen (“wet O_2 ”) as co-reactant at temperatures between 100 and 130 °C. A comprehensive investigation of the Cu_xO ALD process on Ta, TaN, Ru and SiO_2 substrates was already published in [4]. The huge challenge of the subsequent reduction process is a successful conversion of Cu_xO to metallic copper at low temperatures to avoid film agglomeration. Highly efficient reduction results at low temperatures ($T < 130$ °C) were achieved with vapor of formic acid (HCOOH) in connection with Ru substrates, assumedly due to catalytic effects of Ru regarding the decomposition of formic acid towards hydrogen and carbon monoxide [5, 6].

Thus, the Cu ALD films were investigated as seed layers on Ru liners regarding the ECD applicability in comparison to plain Ru as well as compared to Ru coated with sputtered Cu seed layers [7]. Due to the advantageous combination of Ru with ALD Cu seed layers, further investigations were done on typical interconnect patterns formed by electron-beam lithography and reactive ion etching (RIE) of thermal SiO_2

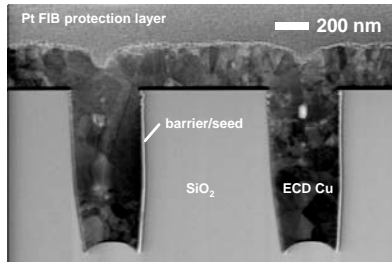


Figure 1. STEM image of interconnect lines nearly perfectly filled with ECD Cu on an ALD Cu / PVD Ru / PVD TaN plating base.

films. The maximum structure aspect ratios are four (width = 200 nm, depth = 800 nm), comparably to Dual Damascene interconnect systems [1]. These patterns were coated with TaN (10 nm) / Ru(10 nm) as diffusion barrier/liner films both by physical vapor deposition (PVD), especially by sputtering. The ECD filling behavior was studied by using scanning electron and scanning transmission electron microscopy (SEM and STEM).

For improving the subsequent HCOOH reduction on arbitrary substrates, a mixture of the established Cu(I) β -diketonate with a small amount (1 mol-%) of the Ru precursor $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\eta^5\text{-C}_7\text{H}_{11})\text{Ru}]$ was applied to introduce the catalytically active Ru into the Cu_xO layers during the ALD process. The ALD process with the Ru-containing precursor as well as the subsequent reduction with HCOOH on TaN, SiO_2 , Ru, Ni, and Co substrates are being studied in more detail using X-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (TOF-SIMS), Auger electron spectroscopy (AES), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), and spectroscopic ellipsometry (SE). Alternatively to the HCOOH reduction, molecular and atomic hydrogen as reducing agent were investigated on Ru, Ni, and Co substrates.

III. RESULTS AND DISCUSSION

A. Cu ECD on Cu ALD seed layers in interconnect patterns

ECD experiments on unpatterned substrates of PVD Ru (100 nm) with Cu ALD (8 nm) seed layers showed the most promising results with respect to the film morphology, roughness, and sheet resistance compared to blanket

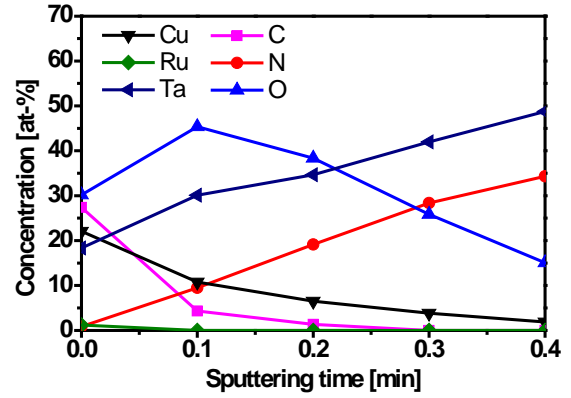
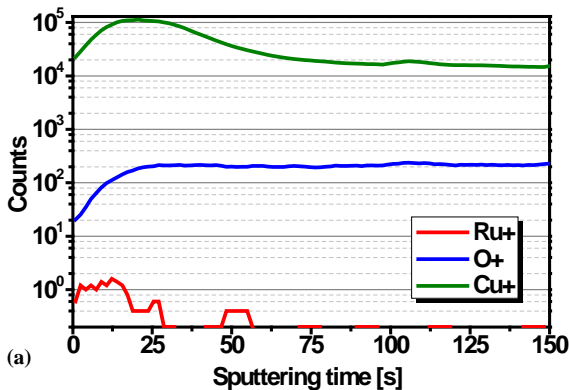


Figure 3. AES depth profile of an ALD Cu_xO film prepared with the Ru-containing Cu precursor on TaN substrate.

Ru (100 nm) as well as PVD Cu (9 nm) / Ru (100 nm) systems [7]. Using a conformal Cu electroplating process on patterned samples without bottom-up filling properties, only porous, grainy Cu was obtained in the test structures directly on Ru. In contrast, adding a < 10 nm thick Cu seed layer to the sputtered Ru (10 nm) / TaN (10 nm) diffusion barrier system, gave much denser ECD Cu films with improved filling behavior as shown in Figure 1. The results suggest that the combination of ALD Cu with Ru can be a viable alternative for liner materials in ULSI electronic devices, especially when ALD-grown barrier materials become prominent.

B. $\text{Cu}_x\text{O}/\text{Cu}$ ALD using Ru-containing precursor

In contrast to the efficient HCOOH reduction of the Cu_xO ALD films to metallic Cu on catalytically active Ru substrates, no significant reduction of Cu (II) and Cu (I) contributions were detectable on TaN [7] and SiO_2 substrates at temperatures below 130 °C by XPS. For improving the subsequent HCOOH reduction on arbitrary substrates at low temperatures, a precursor mixture of the Cu(I) β -diketonate with 1 mol-% of an organometallic Ru precursor was therefore investigated. With this precursor mixture, the ALD process at 120 °C and 0.8-1.5 mbar showed similar growth behavior regarding the growth per cycle (GPC) [4], roughness and film morphology in comparison to the pure Cu(I) β -diketonate precursor, assumedly due to the small amount of Ru precursor. For the

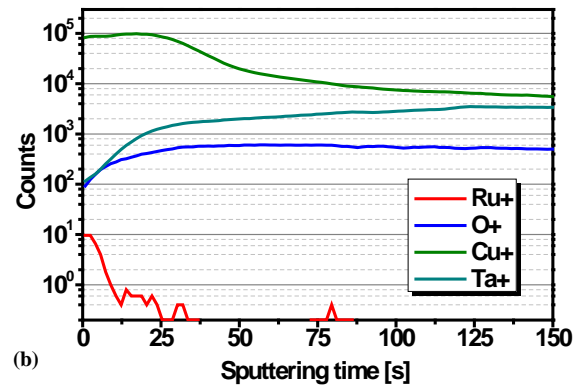


Figure 2. TOF-SIMS analyses (sputter parameters: O_2 , 0.5 keV, 64.6 nA) of PVD Cu_xO without Ru on TiN (a) and ALD Cu_xO with Ru-containing Cu precursor on TaN (b).

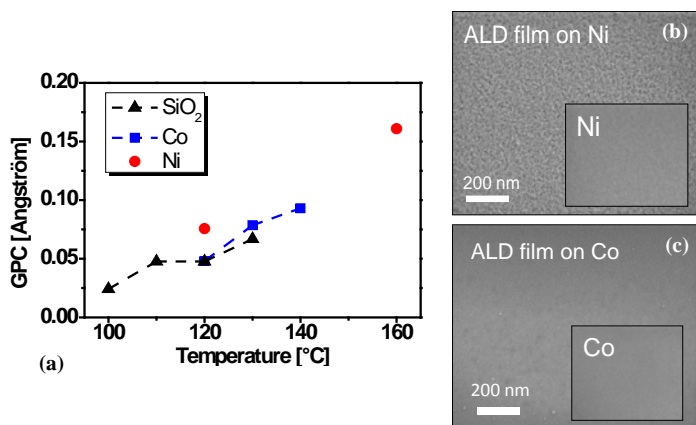


Figure 4. Growth per cycle (GPC) as a function of temperature on SiO₂, Co, and Ni (a) as well as SEM top view investigations of the ALD film growing on Ni (b) and Co (c) in comparison to the substrate.

evaluation of the Ru content introduced into ALD films grown on TaN substrates, TOF-SIMS as well as highly surface sensitive AES analyses were applied. The TOF-SIMS detection limit using a ToF.SIMS 300R is in the range of 10^{18} to 10^{19} at/cm³. Because of the low film thickness (< 5 nm) and the median relative sensitivity factor (RSF) of Ru [8], the proof is quit sophisticated. The enhancement of the Ru signal in comparison to PVD Cu_xO without Ru suggests a successful introduction of Ru (see Figure 2), but the signal strength is below or in the range of the detection limit. However, further investigations by AES using a PHI 670 Auger Nanoprobe without Ar sputtering reveal a clear evidence of Ru in the ALD films. The as-grown ALD films without Ar sputter cleaning consist of carbon (27.3 at-%), copper (22.1 at-%), tantalum (18.4 at-%), ruthenium (1.2 at-%), and nitrogen (0.9 at-%) as shown in Figure 3. Consequently, the Ru content related to the Cu quantity amounts to 5 at-%. The difference to the Ru precursor concentration of 1 mol-% could be due to an enrichment of Ru at the surface or higher adsorption probability of the Ru precursor molecules due to different steric properties or higher reactivity. The huge Ta peak is due to the low ALD film thickness. Furthermore, after a short treatment time of 6 s with Ar ions (3 keV), the Cu signal decreased to 10 % and the Ru signal was no longer detectable. In addition, the ALD process was studied on Co (10 nm) and Ni (10 nm) substrates both prepared by sputtering. The film

nucleation on Ni was stronger in comparison to Co, consequently the GPC determined by spectroscopic ellipsometry was higher and film density on Ni was advanced indicated by SEM top view investigations as shown in Figure 4. Differences regarding the growth characteristics occurred probably due to the catalytic support of Ni substrates.

The HCOOH reduction of Ru-containing ALD films was investigated on TaN and SiO₂ substrates for studying the influence of the catalytic amount of Ru in the ALD films. XPS analyses indicate indeed a clear improvement of the HCOOH reduction on both substrates as shown in Figure 5 for TaN. The core level transition Cu 2p_{3/2} demonstrates a complete removal of the Cu (II) contributions and the enhanced signal in the LMM Auger transition indicates a formation of metallic copper. Residual Cu (I) components are assumedly due to air contact of the samples before the *ex situ* analysis. Furthermore, SEM top view investigations show no film agglomeration on TaN substrates but on SiO₂ substrates due to the higher surface energy. However, the approach of adding a small amount of catalytically active Ru proved successful for improving the HCOOH vapor-phase reduction process subsequent to the thermal ALD of Cu_xO.

C. Molecular and atomic hydrogen reduction of Cu_xO ALD films

Alternatively to the HCOOH reduction, molecular as well as atomic hydrogen as reducing agent were studied on Ru, Ni, and Co substrates by using *in situ* XPS analyses (see Figure 6) and SEM top view investigations. For creation of atomic hydrogen, a hot filament inside the reaction chamber was used. The samples were turned off the filament for avoiding the unwanted thermal radiation. Only a slight reduction of Cu (II) components was detected by applying molecular hydrogen (treatment time 20 min, pressure of 10^{-4} mbar) on Ni substrates. In contrast, a treatment with excited H achieved a complete reduction of Cu (II) contributions as well as almost full removal of the Cu (I) components. However, the SEM top view studies revealed also a change in the morphology, at least regarding the roughness as shown in Figure 7. Similar results were achieved on Ru substrates without changing the film morphology. The *in situ* XPS measurements indicate a full

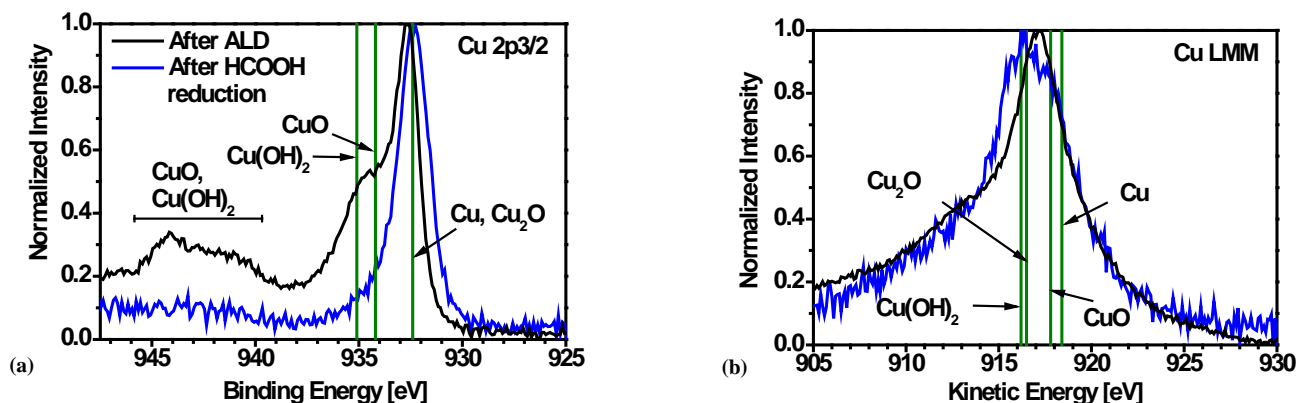


Figure 5. XPS data after ALD (500 cycles, 120 °C, 0.8-1.5 mbar) as well as HCOOH reduction (60 min, 115 °C, 1.3 mbar) on TaN.

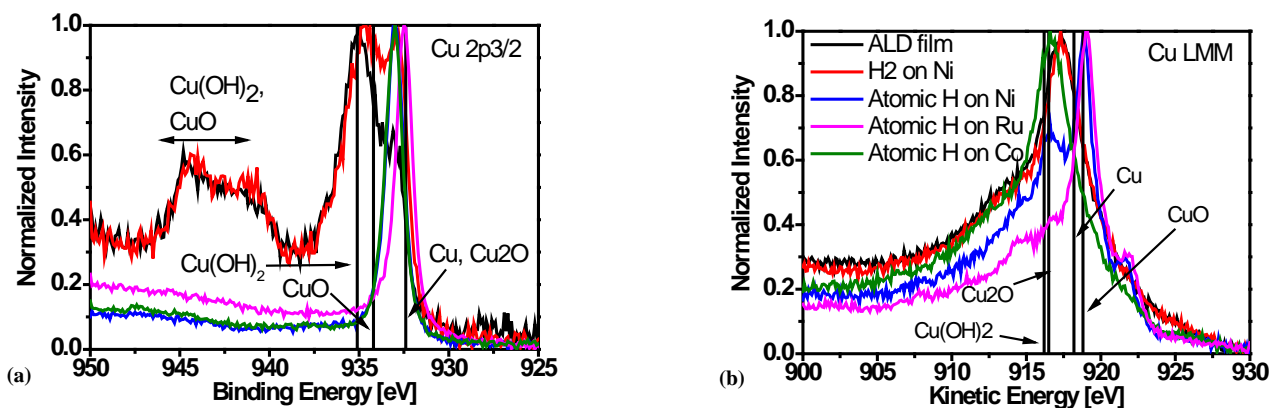


Figure 6. XPS data after ALD (600 cycles, 120 °C, 0.8-1.5 mbar) on Ni, after molecular H reduction on Ni (20 min), and atomic H reduction on Ni (20 min), Ru (40 min) and Co (20 min) at 160 °C and 10^{-4} mbar. The XPS results of the as-grown, unreduced ALD films on Ru and Co are similar to the ALD film on Ni and are therefore not shown.

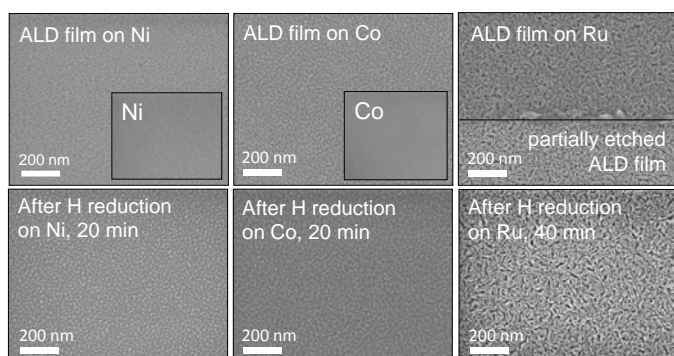


Figure 7. SEM top view investigations of the ALD film growing on Ni, Co, and Ru as well as after an atomic hydrogen treatment at 160 °C and 10^{-4} mbar conversion to metallic copper after an atomic hydrogen treatment of 40 min, compared to XPS data of argon-sputtered bare copper [9]. Unlike on Ni and Ru, no reduction of Cu (I) components was detected on Co substrates. The results again show the catalytic support by Ru as well as Ni substrates regarding the efficiency of the Cu_xO reduction to metallic Cu, offering Ni as a potential further alternative as a liner in ULSI interconnects together with ALD Cu seed layers. Furthermore, the combination of ALD Cu and Ni could be a viable film system for spintronic applications.

IV. CONCLUSION

In summary, the results suggest that the approach of thermal Cu ALD via reduction of Cu_xO films is highly promising regarding applications in ULSI interconnects as seed layer for the subsequent Cu ECD and as non-ferromagnetic spacer layer between ferromagnetic films in GMR sensor elements. Nearly perfectly filled interconnect patterns with ECD Cu were achieved on an ALD Cu/Ru/TaN film stack as seed layer/liner/diffusion barrier plating base. Furthermore, a potential approach for improving subsequent HCOOH reduction of the Cu_xO ALD films to metallic copper films on arbitrary substrates was presented. The successful introduction of a small amount of catalytically active Ru during the ALD significantly improved the HCOOH gas phase reduction on TaN and SiO_2 in comparison to ALD Cu_xO films without Ru. This approach allows the utilization of the Cu

ALD on arbitrary substrates, such as directly on diffusion barriers (e. g. TaN). In addition to the HCOOH reduction, atomic hydrogen as reducing agent was successfully applied on Ru and Ni substrates, but not on Co. Differences occurred assumedly due to the catalytic support of Ru and Ni. Together with the enhanced ALD growth on Ni in comparison to Co, ALD Cu / Ni appears to be a prospective further alternative as a seed layer / liner stack in ULSI interconnects and prospective film system for spintronic or GMR systems.

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