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ARTICLE

Characterization of Thermal Stability of RuMoC Films as Seedless Cu Diffusion Barriers in Damascene Structures for Cu Interconnects

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Abstract: The objective of this study is to test the feasibility of RuMoC films for its application in seedless Cu diffusion barriers of damascene structure. The compatibility with integral circuit (IC) fabrication and thermal stability of RuMoC barriers were investigated. The RuMoC barriers are amorphous at temperatures up to 500 °C, showing great thermal stability. This is because the Ru-C bonds are well preserved at those temperatures, as revealed by XPS results, which hinder the Ru from crystallizing. A Cu plug of good quality was successfully electroplated on RuMoC barriers and filled the trench without seed layer, and the barrier effectively block the diffusion of Cu atom at temperatures up to 500 °C.

Key words: thermal stability; damascene structures; amorphous RuMoC film; seedless diffusion barrier

Nowadays, several millions of devices can be connected and placed on only a few square millimeters of Si chips with satisfactory resistance-capacitance time delay (R-C delay) losses, which can be attributed to the Cu damascene wirings. At present, Cu damascene wirings in the backend of line are usually fabricated by depositing a TaN/Ta bilayer as Cu diffusion barriers and a Cu seed layer followed by a galvanized Cu fill of vias and trenches. As the feature size of the integrated circuit (IC) keeps shrinking, the barrier and seed layer must be constantly decreasing towards to lower dimension to again reduce the R-C delay and to avoid void formation during the Cu fill. Finally, when the required ratio (A/R) of the Cu wire increases to 2.0 for 14 nm technology node and hence the thickness of the diffusion barrier would be reduced to 1.7 nm, as predicted by the International Technology Roadmap for Semiconductors [1], it might not be a good option to use seed layers, nor to adopt TaN/Ta bilayers as barriers since the Ta/TaN barrier at such a limited thickness exhibits a high resistivity up to ~32 μΩ·cm and a columnar grain structure, which would contribute more than 50% to the total resistance and would provide lots of vertical grain boundaries for Cu diffusion, respectively[2–4]. Therefore, a directly platable single Cu diffusion barrier with low resistivity is highly desired.

Noble metal ruthenium (Ru) exhibits low bulk electrical resistivity (~7.1 μΩ·cm) and negligible solid solubility with Cu and hence it can play a role as a Cu diffusion barrier [5,6]. More importantly, Ru can also serve as seed layer for the galvanic fill of vias and trenches, making Ru become a promising candidate for seedless Cu diffusion barriers applied to the devices of next generation[7]. However, a pure Ru become thin film itself has poor barrier performance against Cu diffusion due to its columnar grain structure even at moderate temperatures[8]. Recently, lots of researches were performed on improving the barrier properties of Ru by doping alloying elements into the lattice matrix of Ru films in order to modify its microstructures[5,9-12]. Damayanti et al[11] doped N into Ru films and hence transformed the Ru film structures from

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crystalline to amorphous. It is broadly accepted, however, that the synthesis condition of RuN film is hard to be precisely controlled, principally due to the positive formation enthalpy. Moreover, RuN films exhibit high electrical resistivity (865 μΩ·cm) at room temperature. Hsu et al[13] added Mo into Ru film and hence stuffed the grain boundaries. Nevertheless, the doping of Mo results in the increasing of oxygen content in the film due to the high oxygen affinity rate of Mo atoms.

In this study, RuMoC ternary films were studied as seedless Cu diffusion barrier, enlightened by the finding published by Jansson and Lewin[12] that amorphous ternary materials can be obtained through altering the components by combining one strong (Ti, W, Mo, Ta, etc.) and one weak (Fe, Ru, Ni, Al, etc.) carbide forming metal. A comprehensive study has been carried out in our previous work, showing that RuMoC films exhibited low oxygen content and resistivity along with high thermal stability[14]. The compatibility with IC fabrication and thermal stability of RuMoC barriers were studied to characterize RuMoC films as Cu diffusion barriers in damascene structures for ULSI interconnects.

1 Experiment

RuMoC films with various composition were deposited on Si (111) substrates by magnetron co-sputtering using confocal Ru (99.95%) and MoC (99.95%) targets for the evaluation of residual oxygen content, resistivity and thermal stability. The two targets were tilted to a fixed angle of 55°. The working pressure was 0.35 Pa in a gas atmosphere of Ar and the substrate bias voltage was –50 V. The sputtering power ratio (Ru vs. MoC) vary from 100:0 to 100:50. Cu/RuMoC (5 nm)/ p-SiOC:H/Si stacks in metal-insulator-semiconductor (MIS) structures were fabricated to test the barrier performance of RuMoC films. Details can be found in our previous study [14]. Besides, Cu/RuMoC/p-SiOC:H damascene structure were fabricated by a standard SiO_2/Si_3N_4-based Cu damascene process[15] for the simulation of Cu lines: pattern definition for trench etching was done by lithography machine, followed by the deposition of RuMoC barrier layers with PVD system and the trenches were filled by electrochemical deposition of Cu, and then excessive Cu and barrier material were removed by chemical mechanical polishing (CMP). Finally, samples were annealed at temperatures varied from 300 °C to 500 °C for 1 h in a vacuum furnace at a pressure of 3×10^{-4} Pa.

The sheet resistance of Cu/RuMoC/p-SiOC:H/Si films, before and after annealing, was determined by four-point probe (4PPT) measurements. The change of chemical bond composition in the RuMoC films were measured by X-ray photoelectron spectroscopy (XPS). The crystallographic structures and phase transformation of RuMoC films and Cu/RuMoC/p-SiOC:H/Si stacks were analyzed by the glancing incidence angle (4°) X-ray diffractometer (GIXRD). The microstructures of RuMoC films and the Cu/RuMoC/ p-SiOC:H trench structure were observed with high-resolution transitional electron microscopy (HRTEM), equipped with an X-ray energy dispersive spectrometer (EDS). The electron probe size for STEM-EDS was about 0.7 nm. The details of TEM analysis and the procedures of TEM sample preparation can be found elsewhere[16].

2 Results and Discussion

Table 1 gives an overview of all investigated RuMoC films along with Ru films as reference. The composition of RuMoC films was adjusted by tuning the sputtering ratio between Ru and MoC targets. The RuMoC films show obvious decreasing in oxygen content in comparison with pure Ru films, and the decreasing gets more significant when compared with the RuMo films reported by Wojcik et al [5], where a critical oxygen content up to 19.8% was found. This might be due to two reasons: firstly, MoC exhibits lower oxygen affinity compared with Ru and Mo; on the other hand, part of Ru atoms is bonded with C atoms, and thus O incorporation are partly hindered. In addition, the RuMoC II films exhibit a lower oxygen content than RuMoC I film, indicating the reduction effect on oxygen content from doped MoC strengthen with the increasing of the doping content. However, the increasing in doping content of MoC may augment the resistivity of the RuMoC film for MoC exhibits much higher resistivity than Ru (about 29 μΩ·cm versus 7.1 μΩ·cm).

Fig.1 shows HRTEM micrographs of the as-deposited RuMoC I and RuMoC II films, and the corresponding Fast Fourier Transform (FFT) patterns are shown in the inset images. Inerratic polygons are found in Fig.1a, indicating a polycrystalline structure of RuMoC I film. The FFT pattern, shown in Fig.1a, also demonstrates a polycrystalline structure of RuMoC I film for the white dashed-line circle in the pattern. However, Fig.1b shows an amorphous structure of RuMoC II film, which is confirmed by the corresponding FFT patterns where a broad diffraction ring is found.

XRD analysis was performed to investigate the evolution of phases composition and crystallite structure of the RuMoC I and RuMoC II films with annealing temperatures, and the results are displayed in Fig.2. As shown in Fig.2a, the as-deposited RuMoC I films exhibit a polycrystalline structure, in accordance with Fig.1a. The (100) and (101) crystalline Ru signals dramatically become stronger after the RuMoC I film were annealed at 500 °C. As an actual fact, grain boundaries can be considered as a Cu rapid diffusion path, and thus the RuMoC I film might not serve as Cu diffusion barriers at 500 °C or a higher temperature. On the other hand, the RuMoC II films

Table 1 Composition of investigated RuMoC films

Barrier	Sputtering ratio (Ru:MoC)	Composition/at%			
		Ru	Mo	C	O
Ru	100:0	94.7	0	0	5.3
RuMoC I	100:30	72.5	12.6	13.3	1.6
RuMoC II	100:50	65.1	16.5	17.3	1.1

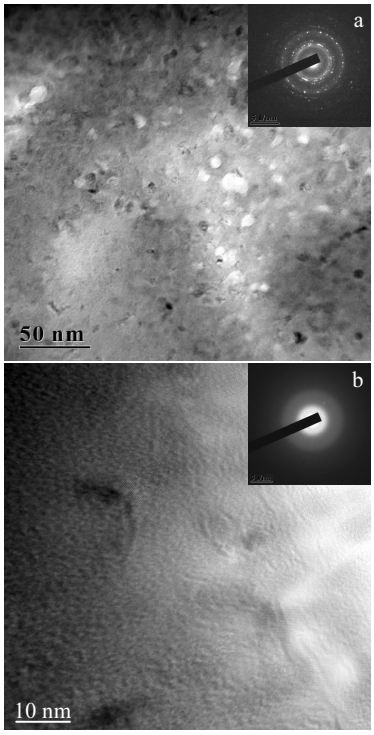

Fig.1 HRTEM micrographs of the as-deposited RuMoC I/Si (a) and RuMoC II/Si (b) films

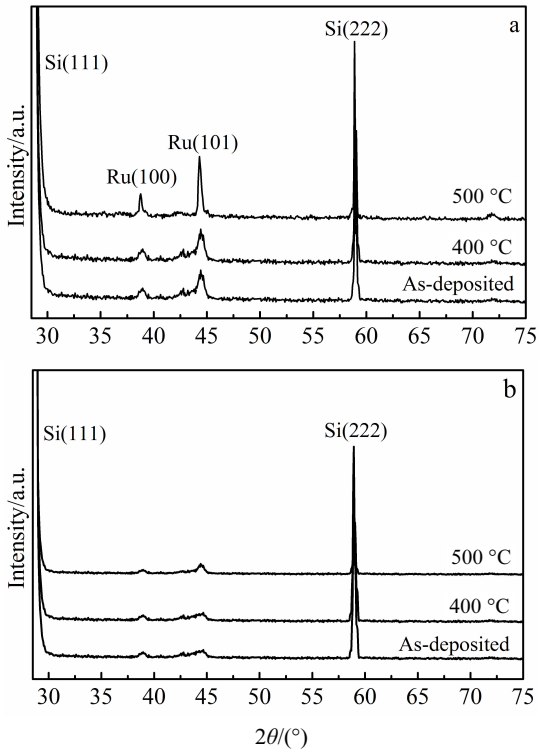

Fig.2 XRD patterns of the RuMoC I/Si (a) and RuMoC II/Si (b), before and after annealing

exhibit an amorphous structure, in accordance with Fig.1b, and the amorphous structure is maintained at temperatures up to 500 °C (see Fig.2b), indicating an excellent thermal stability of RuMoC II film.

The X-ray photoelectron spectroscopy was applied to analyze the change of chemical bonds, before and after annealing at 500 °C. Fig.3 shows the XPS spectra for C 1s, Ru 3d, and O1s taken from RuMoC II films, before and after annealing. Peaks in the XPS core level spectra were fitted with a mixed Gaussian-Lorentzian function, after the background interferences were erased by a Shirley function. As shown in Fig.3a, the C 1s spectra are fitted with C-Ru (280.8 eV) [17], C-Mo (281.8 eV) [18], and C-C (284.9 eV) [19] peaks. Compared with the as-deposited RuMoC II films, the area of the peaks taken from annealed RuMoC II films drop slightly. Typically, the area of C-Ru peak just drops slightly after the films are annealed at 500 °C, which can be a possible explanation for the excellent thermal crystalline stability of RuMoC II films indicated by Fig. 2. The O 1s spectra shown in Fig.3b are fitted with MoO_x (530.5 eV) [20] and RuO_x (531.8 eV) [21] peaks. The area of the peaks increases after the films are annealed, indicating the oxygen contents increase. The Ru 3d spectra are fitted with Ru-C (279.2 eV)[17], Ru (280.2 eV)[17,19,21], and RuO_x (281.8 eV)[20-22] peaks (Fig.3c). After annealing, the area of Ru-C and RuO_x peaks changes synchronously but inversely, supporting that the Ru-C bonds hinder partial Ru atoms from incorporating O atoms. The most encouraging phenomenon is that the C-Ru and C-Mo bonds are well-preserved after the films are annealed at 500 °C, which hinder the Ru from crystallizing contributing to an excellent thermal stability of RuMoC II film[13].

Further investigations about the thermal stability of the Cu/RuMoC II (5 nm)/p-SiOC:H/Si films were also performed. Fig.4 shows the sheet resistance of Cu/barriers/p-SiOC:H/Si stacks after 30 min annealing as a function of the annealing temperature. For all the stack films, the sheet resistances slightly decrease with the increasing of annealing temperature at first, for the reasons of Cu grain growth and defect annihilation of Cu[23]. As the annealing temperature keeps increasing, sheet resistance of the pure Ru barrier rises slightly after 300 °C annealing, and climbs significantly after annealing at 400 °C, while the sheet resistance of Cu/RuMoC I/Si films climbs sharply after 400 °C annealing, indicating the formation of Cu_3Si. In contrast, the sheet resistance of Cu/RuMoC II/p-SiOC:H/Si films stays changeless at temperatures up to 500 °C, suggesting the excellent thermal stability of RuMoC II films. These can be explained by the microstructure change of the RuMoC I and RuMoC II indicated by Fig.2 where the RuMoC I films crystallized significantly while the RuMoC II films remained an amorphous structure at temperatures up to 500 °C.

Besides investigations of samples on blanket Si wafers, it is necessary to study the performance of RuMoC barriers in

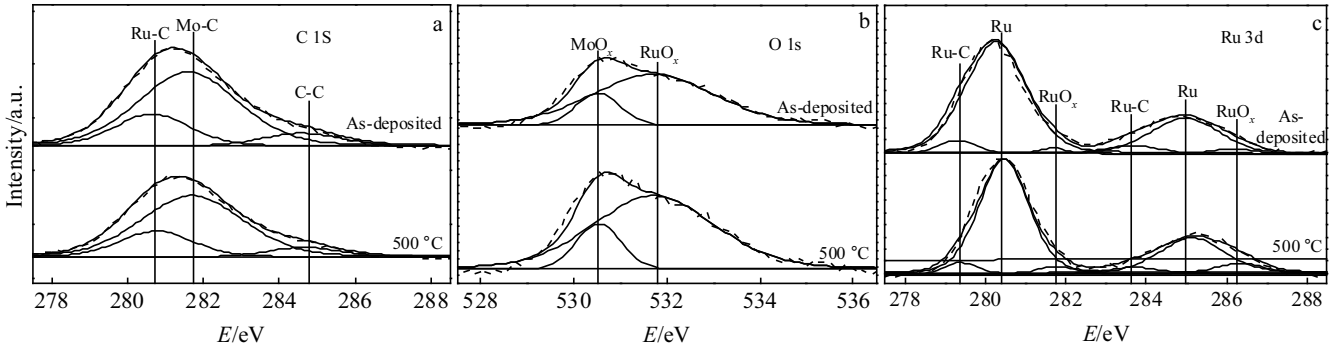

Fig.3 XPS spectra of C 1s (a), O 1s (b), and Ru 3d (c) of RuMoC II/Si films, before and after annealing at 500 °C

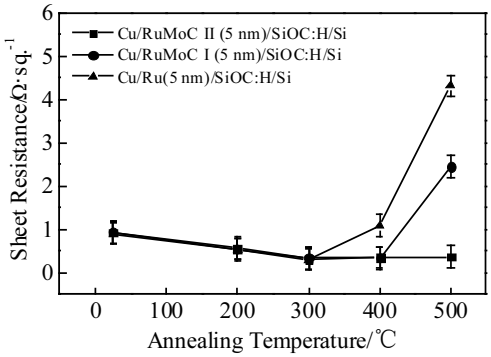

Fig.4 Sheet resistance measured on Cu/barriers (5 nm)/p-SiOC:H/Si as a function of annealing temperature

trench structures. Fig.5 depicts the HRTEM images and EDS depth profiles of Cu/RuMoC II/p-SiOC:H damascene structure after 500 °C annealing. A good quality of Cu plug is deposited on the RuMoC II barrier without seed layer. Good void-free filling is accomplished, and no delamination is found even after annealing at 500 °C. The EDS results shows that the Cu atom counts drop sharply before the p-SiOC:H/Si layer, indicating that the RuMoC II barrier successfully blocks the diffusion of Cu atoms even after annealing at 500 °C. Furthermore, the oxygen atom counts decrease sharply among the RuMoC II layer near the p-SiOC:H/Si layer, suggesting that the RuMoC II barrier also hinder the diffusion of O atoms at temperatures up to 500 °C.

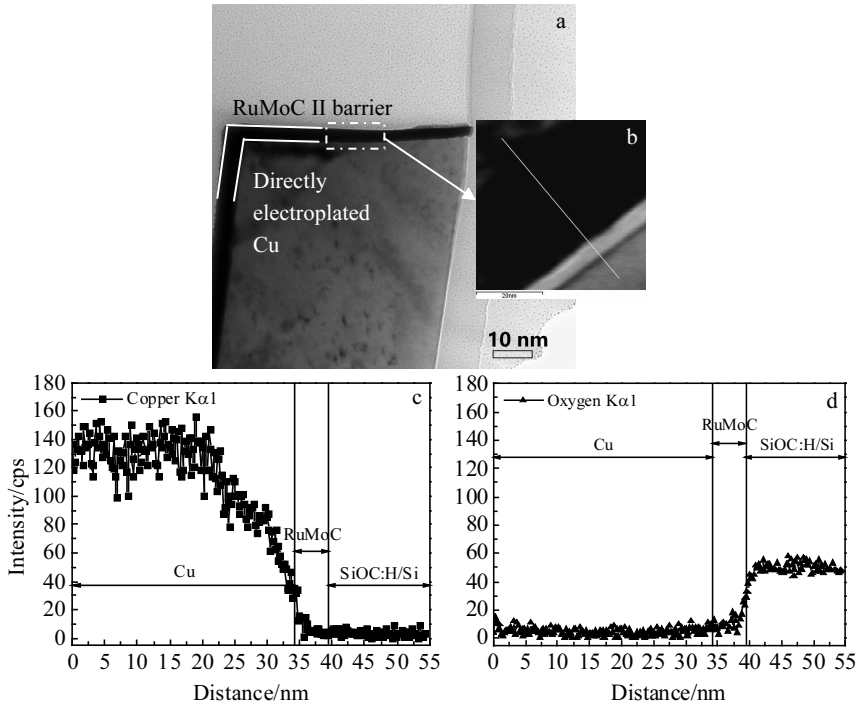

Fig.5 HRTEM images (a, b) and EDS depth profiles (c, d) of electroplated Cu on top of a 5 nm RuMoC II barrier in a damascene structure, annealed at 500 °C

3 Conclusions

1) RuMoC and Cu/RuMoC/p-SiOC:H films can be prepared on blanket Si wafers by magnetron co-sputtering to study the microstructure evolution of RuMoC films.

2) RuMoC II films obtained with sputtering ratios (Ru:MoC) of 100:50 exhibit an amorphous structure at temperatures up to 500 °C. Thus the Cu/RuMoC II/p-SiOC:H films are intact suggested by the sheet resistance results.

3) Ru-C bonds are well-preserved at that temperatures up to 500 °C which hinder the Ru from crystallizing.

4) RuMoC II barrier in Cu/RuMoC/p-SiOC:H damascene structure effectively blocks the diffusion of Cu atom at temperatures up to 500 °C.

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铜互连微结构中无籽晶 RuMoC 扩散阻挡层的稳定性

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摘　要：采用磁控共溅射 Ru 和 MoC 靶，通过调节掺入 MoC 的含量获得非晶态 RuMoC 薄膜，研究了非晶 RuMoC 薄膜的热稳定性。HRTEM 和 XRD 结果表明，在 500 ℃下 RuMoC 薄膜依旧保持非晶结构；XPS 分析结果表明，在该温度下，Ru-C 键依旧保持完好，是 RuMoC 薄膜良好热稳定的关键。此外，研究了非晶 RuMoC 薄膜在大马士革铜互连线微结构中的热稳定性。HRTEM 结果表明，RuMoC 薄膜表面可直接电镀铜，TEM 原位 EDS 结果表明，非晶 RuMoC 薄膜在 500 ℃下依旧成功阻挡了 Cu 原子扩散。

关键词：热稳定性；大马士革结构；非晶 RuMoC 薄膜；无籽晶阻挡层

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