Growth of Ultra-thin Ruthenium and Ruthenium Alloy Films for Copper Barriers

Wen Liao, Daniel Bost, John G. Ekerdt

Department of Chemical Engineering, University of Texas at Austin, Austin, TX, 78712
E-mail: wliao@utexas.edu

Abstract

We report approaches to grow ultrathin Ru films for application as a seed layer and Cu diffusion barrier. For chemical vapor deposition (CVD) with Ru(CO)_{12} we show the role surface hydroxyl groups have in nucleating the Ru islands that grow into a continuous film in a Volmer-Weber process, and how the nucleation density can be increased by applying a CO or NH_{3} overpressure. Thinner continuous films evolve in the presence of a CO overpressure. We report an optimum ammonia overpressure for Ru nucleation and that leads to deposition of smoother Ru thin films. Finally, we report a comparison of amorphous Ru films that are alloyed with P or B and demonstrate 3-nm thick amorphous Ru(B) films function as a Cu diffusion barrier.

1. Introduction

A smooth ultra-thin diffusion barrier/liner is required to prevent copper from diffusing into the interlayer dielectric and electromigration within the vias and wire lines in IC devices. Ruthenium is a promising material in future designs due to its high conductivity, superior thermodynamic and chemical stability, and the low solubility with Cu. To minimize Cu diffusion through grain boundaries and improve Cu electroplating behavior on films, small nanocrystalline grain size and a smooth film surface are desired in the semiconductor industry. Alternately, amorphous films that lack grain boundaries should also work as a diffusion barrier.

2. Experiment

Growth experiments are performed in a spherical cold-wall stainless steel CVD chamber. The metal precursor is preheated in a sealed tube and showered 1 inch above the substrate. An in situ X-ray photoelectron spectrometer, connected to the CVD vessel with an ultra-high vacuum transfer line, was used to monitor carbon content in the film after 60 s Ar ion sputtering. For ex situ characterization, the surface images for particle density and size distribution analysis were taken by scanning electron microscopy (SEM). Atomic force microscopy (AFM) was used to measure roughness. Film thickness was measured by X-ray reflectivity (XRR). Film crystallinity of films was established using X-ray diffraction (XRD).

3. Results

3.1 Pretreatment of silica substrate

Zhuravlev demonstrated the distribution of the surface silanol groups and siloxane bridges as a function of temperature of pretreatment. The Ru(CO)_{12} precursor is reasoned to react with SiO_{2} hydroxyl groups forming unstable HRuO(OSi) grafted clusters that thermally decompose to metallic ruthenium. HRuO(OSi) can also continue to react with SiOH groups. Ru(CO)_{12} is reasoned to thermally decompose directly to give Ru above 150 °C once the SiOH groups are consumed. In Figure 1, the silica substrates are pre-annealed at temperatures from 200 to 920 °C, and are then exposed the same nucleation condition at 130 °C when free hydroxyl groups are the unique nucleation sites. The Ru nucleation density increases as the silica substrates are pre-annealed at temperatures from 200 to 400 °C, and decreases at temperatures from 400 to 920 °C, consistent with Zhuravlev model of free hydroxyl groups over this temperature range. This substrate pretreatment can be used to enhance the initial nucleation density, however it is limited by the surface chemistry of SiO_{2}.

3.2 CO inhibitor optimization on Ru nucleation

Ruthenium was deposited on SiO_{2}/Si(001) substrates using Ru(CO)_{12} with and without an overpressure of CO. Carbon monoxide was employed to inhibit the growth of previously-nucleated islands to force the formation of additional nuclei (Fig. 2). Carbon monoxide also competed with the precursor for free hydroxyl sites on SiO_{2} sites where precursor adsorption and decomposition is favored. The nucleation density decreases with increasing overpressure when CO and precursor are injected simultaneously from the beginning; in this case, CO blocks the free hydroxyls where the Ru precursor dissociates. When CO is introduced for 5 min to the CVD chamber after a 10 min period of deposition without CO, the maximum nucleation density was achieved (16.4×10^{11}/cm^{2}), which is twice as much as the Ru particle density found for 15 min deposition without added CO (Fig. 3). After 10 min of growth hydroxyl groups have mostly reacted and the injected CO adsorbs on Ru nanoparticles, inhibiting growth and forcing additional Ru nucleation on the SiO_{2} substrate. Growth was extended to 2 hr to explore the influence of CO on ultra-thin Ru film characteristics. CO addition to CVD with Ru(CO)_{12} at the proper timing and at the effective partial pressure reduces the film growth rate, surface roughness and nanocrystalline grain size.
3.3 NH₃ inhibitor growth on Ru nucleation and thin film deposition.

Ru(CO)₁₂ reaction on SiO₂/Si(001) substrates at 448 K during CVD with and without an overpressure of NH₃ was studied to see if NH₃ could affect the ruthenium nucleation process and thin film properties. NH₃ was used at partial pressures from 0 to 27.75 mTorr. At moderate partial pressure, NH₃ adsorbs on the previously-nucleated Ru islands reversibly to force the formation of additional nuclei. At too high overpressure, the NH₃ dissociates and N poisons the Ru surface resulting in thinner and rougher films (Fig. 4). The maximum nucleation density was realized (8.1×10¹¹/cm²) when 5.25 mTorr NH₃ is introduced to the CVD chamber, significantly greater than the Ru particle density deposited without adding NH₃ (3.1×10¹¹/cm²) (Fig. 5). Growth was extended to 1 hr to explore the influence of ammonia on ultrathin Ru film characteristics. The film grown with 5.25 mTorr NH₃ was considerably smoother than the film grown without NH₃ (Fig. 6) and there is no detectable carbon or nitrogen contamination in the thin metallic Ru films after post-growth annealing.

3.4 Amorphous ruthenium-phosphorus and ruthenium-boron alloy thin films.

First principles density-functional calculations are presented revealing that Ru(P) and Ru(B) alloys with moderate P (B) content can result in glassy structures exhibiting short and medium range order. The low P (B) content region amorphous phases are energetically more favorable than the crystalline counterparts for the Ru(P) and Ru(B) alloys above ~20 at.% P and ~10 at.% B by calculation (Fig. 7) and experiment (Fig. 8). Very low PH₃ partial pressures (~ 0.13 mPa) and a sequenced addition process are required to allow accumulated P diffusing into the Ru(P) film during growth. XRR and AFM indicate that films of good continuity and smoothness can be grown by CVD in the 3 nm thickness range. XRD shows the amorphous phase to be stable for annealing to 400°C for 3 hr. Electric field stress tests to failure for Cu/Ru(P)/SiO₂/Si stacks indicate that low-carbon Ru(P) barrier films function at least as well as their higher-carbon counterparts as Cu barriers and better than Ta/TaN stacks of similar thickness grown for comparison purposes (Fig. 9). The growth of ultrathin (3nm) amorphous Ru(B) alloy films of varying B concentration via chemical vapor deposition is explored using Ru(CO)₁₂ and B₂H₆ as the Ru and B sources, respectively. Experiments reveal the films grown at 250°C are amorphous at B contents in excess of 15 at.% and polycrystalline below 10 at.% B, consistent with first-principles predictions (Fig. 8). Amorphous Ru(B) films remain amorphous following annealing at 450°C and become polycrystalline at 500°C. Electric field stress tests to failure for Cu/3-nm Ru(B)/SiO₂/Si stacks are used to indicate suitability of Ru(B) as a copper diffusion barrier layer (Fig. 9).

4. Summary

Pre-annealing at 400°C gives highest nucleation density of Ru(CO)₁₂ due to the maximum free hydroxyl groups on SiO₂ surface. CO or NH₃ adsorb on Ru nanoparticles and force additional Ru island formation to the enhance nucleation density. a-Ru(B) and a-Ru(P) amorphous films produced using B₂H₆ and PH₃ appear promising as a liner material in technology node sizes requiring liners at < 5 nm thickness.

Acknowledgement

This work was supported by the National Science Foundation (Award CBET-1160195).

References


Fig. 1 The diagram of nucleation density vs. substrate pretreated temperatures from 200 to 920 °C and the corresponding SEM images at each point following CVD with Ru(CO)₁₂ at 130°C.
Fig. 2 Schematic description of the inhibitor effect during CVD nucleation.

Fig. 3 Left: SEM of CO effect on Ru Nucleation at different sequences using Ru(CO)$_{12}$ precursor. Red box: highest density route; blue box: smallest nuclei route. Top: chemical schematic diagram.

Fig. 4 Schematic diagram of NH$_3$ addition to Ru CVD compared to deposition without NH$_3$.

Fig. 5 Ru nanoparticle density (●), and diameter distribution (■) vs. NH$_3$ partial pressure. Top left: SEM of nucleation without NH$_3$; right: SEM of nucleation with optimal NH$_3$ addition.

Fig. 6 Ru film roughness vs. NH$_3$ partial pressure. Top left: AFM of film without NH$_3$; right: AFM of film with optimal NH$_3$ addition.

Fig. 7 Variation in the mixing enthalpy for amorphous and crystalline Ru(P) and Ru(B) alloys as a function of P(B) content (at.%). The values for amorphous alloys are averaged based on 3 different 64-atom supercells.

Fig. 8 Top: resistivity of various Ru(P) films vs P content. Bottom: resistivity of various Ru(B) films vs B content.

Fig. 9 □ is the median failure time of the 3nm 15 at% B Ru(B) film. ○ is a 3nm amorphous Ru(P) film. ● is a 5nm Ru crystalline film with no P, grown for comparison. ■ is a 5nm TaN film grown for comparison.