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Roughness Analysis of CVD Cu Films on Different Substrates by AFM Imaging

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The roughness analysis of chemical vapor deposition (CVD) of copper (Cu) thin films on various substrates with and without seed layers was studied using atomic force microscopy (AFM). The effect of the seed layers on the film morphology was investigated, and none of the seed layers on the substrates improved the film morphology compared with TiN.

Keywords AFM, CVD, roughness measurement, Cu

1. Introduction

Aluminum (Al) and its alloys have serious limitations in submicron devices, and they cause functionality and reliability problems in ultra large scale integrated (ULSI) and very large scale integrated (VLSI) circuits. Other metallization materials, such as Au, Ag, and Cu, are studied seriously as candidates for replacing aluminum. Among those materials, copper (Cu) has received much attention due to its low resistivity (1.67 μΩcm), high electromigration resistance, and high melting temperature compared with Al or its alloys.[1] So far, a number of studies have been made on the chemical vapor deposition (CVD) of Cu. It has been reported that the processing condition and the system greatly affect the resistivity, purity, selectivity, and morphology of the films. It has also been reported that the surface of CVD Cu films are almost always very rough. Roughness is one of the most important physical parameters for the film quality and it is also important from the viewpoint of giant magnetoresistance (GMR). Experiments show that mixed interfaces decrease GMR effect very sharply.[2] Therefore, obtaining a smooth film surface also plays a significant role for GMR applications.

In this work, the roughness analysis of the CVD Cu films on a number of modified substrates of fire polished glass (FPG) and titanium nitride (TiN) coated on Si wafers was investigated. In this investigation, the materials used for the seed layer were Cu, Cr, and Au. The smoothness of films was determined by the roughness measurements on an atomic force microscope (AFM).[3]

2. Experimental Procedures

In this experiment, two different types of substrates, FPG and TiN, were used. The FPG substrates 11 × 22 mm^2 in size are microscope slides treated with a number of chemical cleaning steps. The slides were immersed in a beaker filled with methanol and they were kept in an ultrasonic cleaner for 30 min and then washed by distilled water. The same cleaning process was repeated by using acetone. By using another beaker filled with distilled water, slides were kept inside an ultrasonic cleaning instrument for 30 min again. The clean samples were blown dry with high-purity N_2 and then immediately fire polished with a propane torch. Thus, the smooth and impurity-free surface was obtained to deposit Cu CVD and seed layers. Cr, Cu, and Au seed layers 30 Å thick were deposited by the physical vapor deposition (PVD) technique on FPG substrates. Metal evaporations were carried out in a cryogenically pumped vacuum system with a base pressure better than 10^{-6} torr. Cr, Cu, and Au wires were thermally evaporated on FPG substrates affixed to an aluminum holder. The film thickness was controlled with a quartz crystal microbalance. The deposition rates for all samples were 0.5 Å s^{-1}. By using a batch method, 15 samples were deposited at one time. Therefore, the same evaporation conditions were obtained for all samples. Once evaporation was completed, the evaporation chamber was backfilled with high-purity N_2 gas, and the samples prepared for AFM measurement and the CVD process. In addition, to provide adhesion and uniform surface distribution, a film of Cr (30 Å) was deposited on FPG followed by an Au film (30 Å)

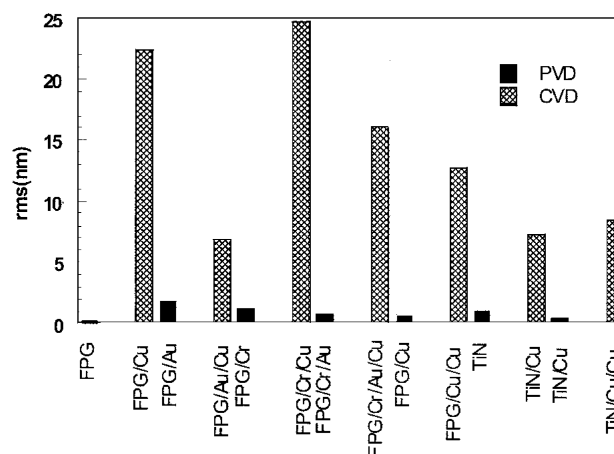

Fig. 1 The root mean square (rms) values of PVD and CVD Cu films on fire polished glass and TiN substrates

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by evaporation technique. In a similar way, 30 Å thick Cu films evaporated on the TiN/Si substrates (Wafernet Inc., San Jose, CA). TiN/Si substrates are Si(100) wafers with a 500 Å TiN barrier layer deposited by sputtering technique.

An in-house warm wall low pressure CVD system was used to deposit Cu films on predeposited substrates (Cr, Cu, Au, and Au/Cr) and bare FPG and TiN substrates. Prior to Cu deposition, TiN/Si substrates were cut by a diamond-tipped cutter into square plates approximately 1.5 × 17 mm^2. The cut substrates were rinsed with trichloroethylene and boiled for 20 min. After 20 min, the substrates were transferred to a beaker filled with distilled water and stirred for 5 min. The same cleaning procedure was also repeated using acetone, and finally substrates were dried by nitrogen stream. The dark green copper hexafluroacetylacetonate, Cu (hfac), was used as a precursor. The substrates were heated to the desired temperatures by a car-

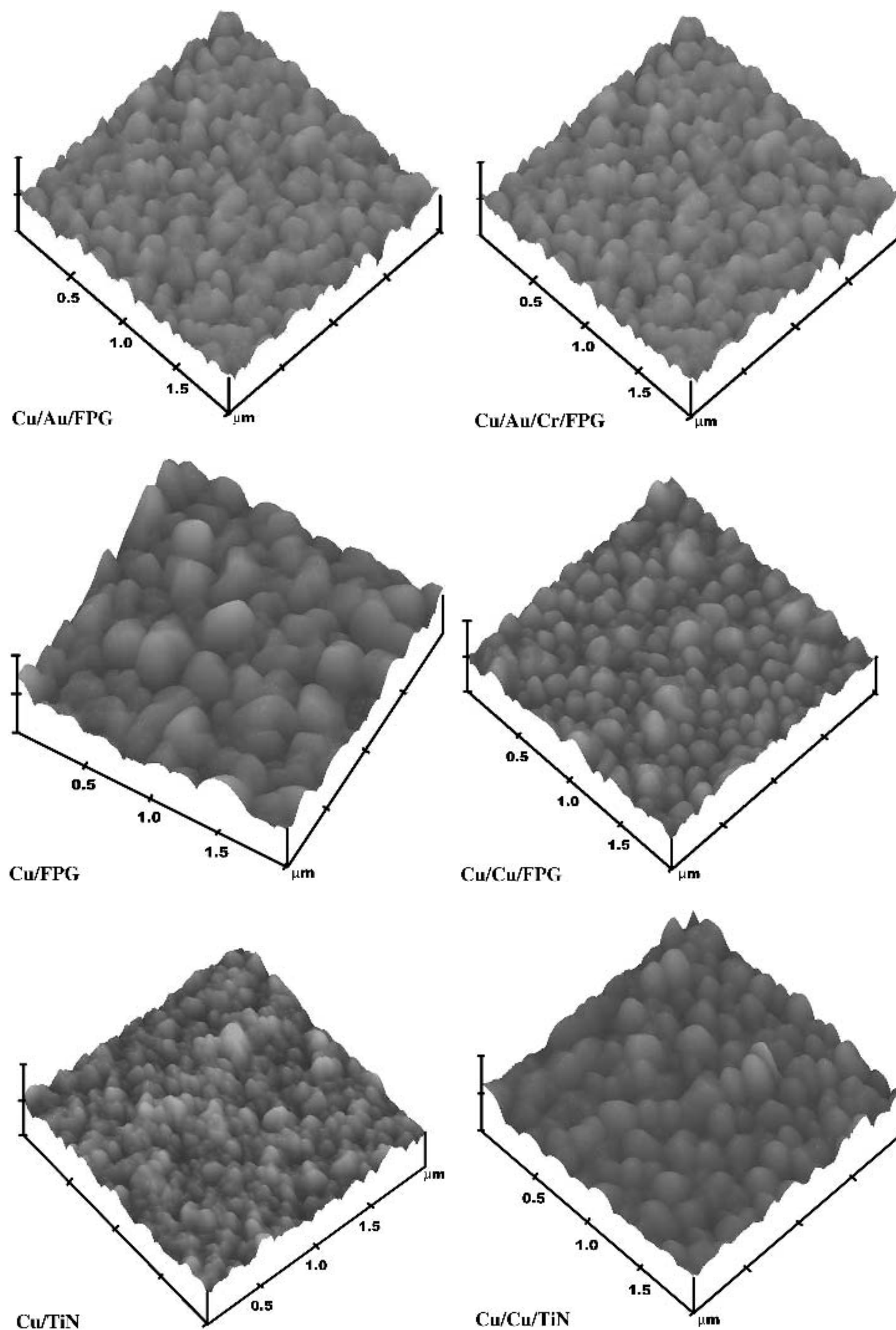

Fig. 2 2 × 2 μm AFM images of CVD Cu films deposited on various seed layers

Table 1 Summary of the Experimental Conditions Used for CVD of Copper

Substrate temperature	300 °C
$Cu(hfac)_2$ reservoir temperature	90 °C
$Cu(hfac)_2$ partial pressure	2-4 torr
Growth time	2 min
Total pressure inside the reactor	40-80 torr
Flow rate of H_2	20-40 sccm
Co-reactant partial pressure	8-9 torr

tridge heater, E1A53-G12C14 (Watlow Firerod, St. Louis, MO). A thermocouple (Omega KMTSS-062G-6, Stamford, CT) was placed on the substrate to measure substrate surface temperature. H_2 was used as a carrier gas and isopropanol (i-PrOH) as a co-reactant. The Cu $(hfac)_2$ precursor was heated to 90 °C by an oil bath. The precursor reservoir and delivery gas line was heated to 120 °C by heating tapes to prevent any condensation of Cu $(hfac)_2$ on the flow system. Mass flow controllers (MKS Inst., Andover, MA, 1159-B, 50 and 100 sccm capacity) were used to meter all gas flow rates. The pressure in the system was regulated by an Alcatel 2004-A (New York, NY) model rotary vacuum pump. A Varian (Plainfield, NJ) 6543-25-045 Model manometer connected to digital readout (Varian DV 1500) was used to maintain the pressure. The operating conditions of CVD Cu films used in this work are summarized in Table 1. Detailed experimental conditions are given in Ref. 4. To investigate the effect of seed layers on the film morphology, there was an attempt to obtain the same operating conditions for all samples.

The surface morphology of the films was characterized using an AFM (Digital Instruments, New York, NY Nanoscope III apparatus). Root mean square (rms) values obtained from 2 × 2 μm scan areas were used to determine the roughness of the films. In measurements, a contact mode was used with pyramidal silicon nitride tips with a force constant of 0.06-0.58 Nm^{-1}. Images presented here were low pass filtered and flattened using the manufacturer's software. All images were obtained in air. A four-probe method was used to measure resistance of the films. In this work, only the results of the films whose resistivities were between 2 and 5 μΩcm were reported for roughness analysis. The thickness of the films was measured by two different techniques. The weight of the samples was measured before and after Cu deposition by using a microbalance (CHAN CN2000). The thickness of the samples was calculated by using weight change of samples after deposition. A detailed calculation can be seen elsewhere.[4] The surface profiler (Tencor Alpha step 200, San Jose, CA) was also used for precise measurement of step height on samples. The measurement probe is a needle stylus surface profiler. For measurement, two perpendicular lines were cut to the TiN layer through the film with a razor blade. The profiler was passed across the lines, and an average of the readings was recorded as sample thickness. In this work, the thickness values of samples scanned in AFM were measured between 0.05μm and 0.17μm. For roughness comparison, the same deposition time (2 min) was used for all samples.

3. Results and Discussion

Figure 1 shows the rms values of PVD and CVD Cu films on PVD seed layers. For comparison, the rms values of bare FPG and TiN are also shown in Fig. 1. Surface morphologies of CVD Cu films examined by AFM are given in Fig. 2. As shown in Fig. 1, the rms values of CVD copper films on bare FPG and on seed layered FPG are very high compared with those on bare TiN and on Cu/TiN (except CVD Cu on Au/FPG). Moreover, as indicated in Fig. 1, the rms values of CVD Cu films on TiN with seed layer Cu are higher than those of TiN without seed layers. In addition, rms values of CVD Cu films on Au and Cu seed layers are low, but they are very high on the Cr seed layer. Similar results have been reported by Awaya et al.[5] According to them, CVD Cu films on the Cr seed layer were not smooth, but they were smooth on the Cu seed layer. In addition, Kim et al. reported that the surface of CVD Cu films on Au seed layers was smooth.[6] The reason for this might be related to surface free energy differences between Cr ($\gamma = 2.056$ J/m^2) and Au ($\gamma = 1.33$ J/m^2).[7] Because γ_{Cr} is greater than γ_{Au}, Cr does not wet the Cu surface. In addition, the Cu seeded layers have catalytic activities for CVD Cu nucleation; therefore, the nucleation and growth of the Cu grains on the Cu seeded substrates proceed further than those on the unseeded ones. Moreover, the presence of a seeding layer can supply more nuclei.

4. Conclusions

The effects of seed layers on CVD Cu film morphology on various substrates were investigated. Though smooth CVD Cu films were obtained in the presence of Cu and Au seed layers, none of the layers on the substrates improved the film morphology compared to that of TiN.

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References

1. P.L. Pai and C.H. Ting: "Selective Electroless Copper for VLSI Interconnection," *IEEE Electron Devices Lett.,* 1989, *10*(9), pp. 423-25.
2. M. Suzuki and Y. Taga: "Giant Magnetoresistance in Co/Cu Superlattices with Mixed Interfaces," *J. Appl. Phys. Lett.,* 1993, *74*(7), pp. 4660-63.
3. G. Binnig, C.F. Quate, and Ch. Gerber: "Atomic Force Microscope," *Phys. Rev. Lett.,* 1986, *56,* pp. 930-33.
4. R. Thiruvenkatachari: "Chemical Vapor Deposition of Copper Thin Films," M.S. Thesis, Louisiana State University, Baton Rouge, LA, 2000.
5. N. Awaya and Y. Arita: "Double Level Copper Interconnections Using Selective Copper CVD," *J. Electron. Mater.* 1992, *21*(10), pp. 959-64.
6. J.Y. Kim, P.J. Reucroft, and D.K. Park: "Nucleation and Growth Mechanism of Copper MOCVD Film on Au/Si Substrates," *Thin Solid Films,* 1996, *289,* pp. 184-91.
7. L.Z. Mezey and J. Giber: "The Surface Free-Energies of Solid Chemical Elements Calculations From Internal Free Enthalpies of Atomization," *Jpn. J. App. Phys.,* 1982, *21*(11), pp. 1569-71.