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Nucleation and Adhesion of ALD Copper on Cobalt Adhesion Layers and Tungsten Nitride Diffusion Barriers

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Atomic layer deposition (ALD) was used to make conformal diffusion barrier layers of WN, adhesion layers of Co, and seed layers of Cu. Transmission electron microscopy and atomic force microscopy were used to study the nucleation of these layers. WN and Co nucleated uniformly as continuous layers. Cu nucleated as discontinuous islands on SiO_2, Si_3N_4, and WN, but as a continuous, nanocrystalline layer on Co/WN. Electrical continuity was found for Cu/Co layers with a thickness under 2 nm. Extremely strong adhesion (>31 J/m^2) was measured for the Cu/Co/WN/SiO_2 structure, more than five times higher than the Cu/Ta/TaN_x/SiO_2 structures currently used for interconnects.
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Microprocessor technology now relies on copper for most of its electrical interconnections. Because of the high diffusivity of copper, diffusion barriers are needed to keep the copper from diffusing into the insulators and silicon semiconductors, in which copper would degrade or destroy performance. Sputtered tantalum nitride (TaN_x) generally serves as the copper diffusion barrier. Another problem with copper is that it has weak adhesion to most other materials, including TaN_x. Thus an adhesion-enhancing layer of sputtered tantalum metal (Ta) is placed between the TaN_x and the copper. A thin layer of sputtered copper serves as the seed for electroplating of the bulk of the copper interconnections.

The sputtering technology for depositing seed layers of copper is experiencing difficulty in placing the copper within increasingly narrow trenches and vias.[1] If the copper seed layer has any gaps in its continuity, then a void may remain after the electrochemical filling of the conductor. Such a void may cause high resistance or even an open circuit. This problem arises because of the limited step coverage that can be achieved using sputtering.

Atomic layer deposition (ALD)[2] is able to deposit films that are completely conformal even in very narrow trenches and vias.[3] ALD is a variation on chemical vapor deposition (CVD) in which two reactant vapors are supplied alternately to a surface. In order to achieve the conformality, each of the vapors must have a self-limiting reaction with the surface on which the other reactant has already chemisorbed. One of the reactants must also have a self-limited reaction with the substrate, in order to begin the deposition process.

To apply ALD to the formation of conformal barrier/seed layers, suitable reactant pairs need to be identified. Ta_3N_5 made by reaction of ammonia and pentakis(dimethylamido)tantalum[4] is a good diffusion barrier,[5] but has very high electrical resistivity. More conductive ALD TaN_x can be made using atomic hydrogen as a reactant;[6] however, ALD reactors supplying atomic hydrogen are more complicated than thermal ALD reactors. ALD Ta has only been made by using a chloride-based Ta precursor, typically reacted with atomic hydrogen.[7] However, chloride precursors and their HCl reaction byproducts are too corrosive to be compatible with Cu technologies. TaF_5 is not corrosive to copper, but its by-product hydrogen fluoride is corrosive to SiO_2.[8] Hence, a Ta adhesion-enhancing layer is not readily available by ALD. Finally, Cu deposited from fluorinated copper precursors has shown weak adhesion[9] and poor electromigration resistance[10] when deposited on Ta. For these reasons, suitable ALD processes for making the traditional Cu/Ta/TaN_x seed/barrier interconnect structure are not known.

In this letter we evaluate Cu/Co/WN as an alternative intercon-

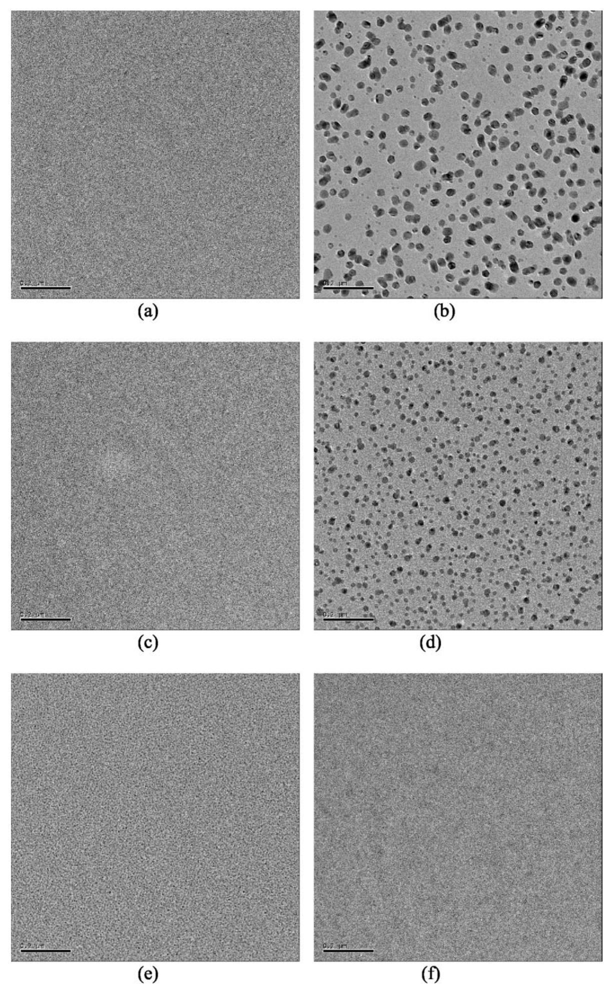

Figure 1. TEM images, scale bars: 200 nm. (a) Bare SiO_2 membrane. (b) 6 nm of ALD Cu on SiO_2 membrane. The copper islands are not connected electrically. (c) WN (3 nm)/SiO_2. WN film nucleates uniformly on SiO_2 membrane. (d) Cu (1.4 nm)/WN (3 nm)/SiO_2. The separate copper islands are connected electrically only by the WN. (e) Co (2 nm)/WN (3 nm)/SiO_2, continuous cobalt film nucleates well on WN surface. (f) Cu (1.4 nm)/Co (2 nm)/WN (3 nm)/SiO_2, continuous copper film nucleates well on Co surface.

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Table I. Sheet resistances of different structures, in k$\Omega/\square$.

Sheet resistance	Si_3N_4 or SiO_2	WN (3 nm) Si_3N_4	Co (2 nm)/ WN (3 nm)Si_3N_4
Without Cu	$>10^5$	17.0	1.42
1 day	$>10^5$		
5 days	$>10^5$		1.78, + 26%
7 days	$>10^5$	25.1, + 40%	
5 weeks	$>10^5$	27.3, + 60%	2.03, + 43%
With Cu (30 cycles)	$>10^5$	15.3	1.01
3 days	$>10^5$	18.8, + 20%	
7 days	$>10^5$	19.4, + 27%	
5 weeks	$>10^5$	22.4, + 46%	1.56, 55%

nect structure for which suitable ALD processes are known. Amorphous ALD WN has already been shown to be an excellent diffusion barrier even at a thickness of only 1.5 nm.[11] Conformality of each of these three layers has already been demonstrated in holes with aspect ratios over 100:1, far exceeding the requirements of the *Roadmap*.[12] Furthermore, these thermal ALD processes can operate without deposition on reactor walls, eliminating the need for cleaning off wall deposits of these metals, which are difficult to remove by chemical etching. Here we demonstrate electrical continuity and extremely strong adhesion for interconnect structures consisting of ALD Cu(1.4 nm)/Co(2 nm)/WN(3 nm)/SiO_2. Adhesion for the ALD Cu/Co/WN/SiO_2 is found to be more than five times higher than that of the currently used Cu/Ta/TaN_x/SiO_2 structure.

Substrates for transmission electron microscopy (TEM) were commercial, thin, electron-transparent SiO_2 membranes spanning holes in a Ni grid (SPI, Inc.). For electrical, atomic force microscopy (AFM), adhesion measurements, and Rutherford backscattering spectra (RBS), substrates of SiO_2 or Si_3N_4 films on silicon wafers were used. Organic contamination on these surfaces was removed by exposure to a mercury UV lamp in air until the surfaces

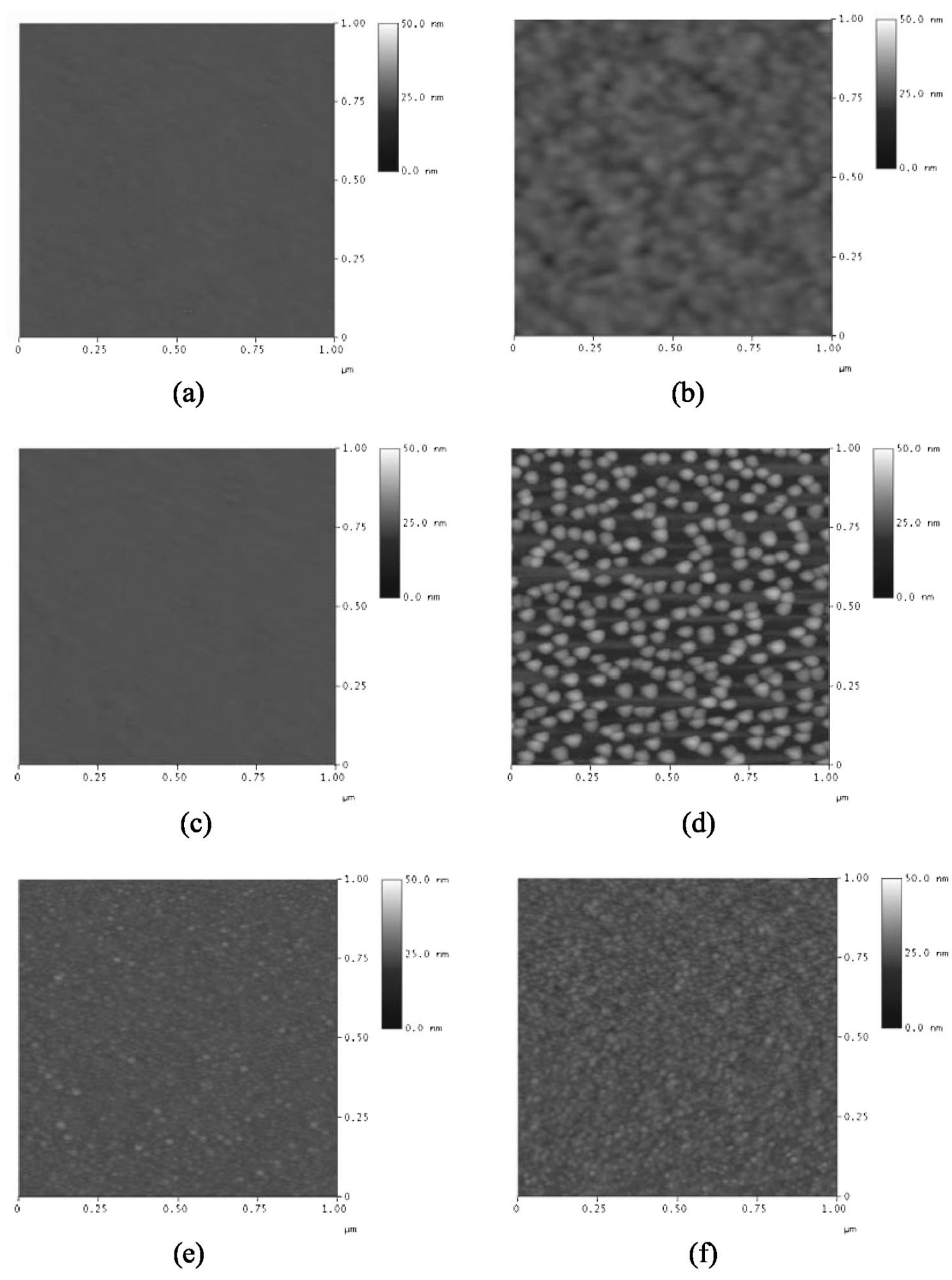

Figure 2. Plane-view AFM images (lettering as in Fig. 1). RMS roughness values: (a) 0.3, (b) 1.7, (c) 0.4, (d) 5.5, (e) 1.0, and (f) 1.6 nm.

became hydrophilic. This oxidation treatment should make the surface of the Si_3N_4 chemically equivalent to a SiO_2 surface. The results reported below did not show any significant differences between films grown on UV-ozone treated Si_3N_4 and those grown on SiO_2.

ALD WN was deposited from bis(*tert*-butylimido) bis(dimethylamido)tungsten and ammonia at 380°C.[13] ALD cobalt was deposited by 100 alternating exposures to bis (N, N'-diisopropylacetamidinato)cobalt(II) and molecular hydrogen gas at 300°C.[14] Copper was deposited by ALD using 30 alternating exposures to (N, N'-di-*sec*-butylacetamidinato)copper(I) vapor[15] and molecular hydrogen gas at a substrate temperature of 190°C. Samples remained in the same ALD reactor during all three depositions. During the time that the furnace was cooling from one temperature to the next, high-purity nitrogen and hydrogen flowed over the samples. Samples were cooled to near room temperature before removal into ambient air. TEM samples were then examined in plane view through the SiO_2 membrane. AFM data were collected in the tapping mode in air on Si_3N_4/Si substrates placed close to the TEM grids during deposition. Sheet resistances were measured with a Veeco four-point probe. Adhesion energies were evaluated by the four-point bend method, as described previously.[16] The samples for adhesion energy measurements had 2 nm of ALD Co and 25 nm of ALD Cu. For some of the adhesion samples, copper (0.4 μm thick) was also sputtered on top of the ALD Cu before bonding the samples to a second piece of silicon with high-strength epoxy. X-ray photoelectron spectroscopy (XPS) and RBS were used to identify which interface failed during the measurement of the adhesion energy.

TEM of ALD Cu (30 cycles) grown directly on the oxidized SiO_2 membranes showed islands of varying sizes (Fig. 1b). These Cu/SiO_2 samples are insulating, showing that these Cu islands are separated by bare SiO_2 surface. RBS showed 4.86×10^{16} copper atom/cm^2, corresponding to an average thickness of 5.7 nm, assuming the bulk density for copper. TEM of WN (Fig. 1c) demonstrated amorphous films that are as featureless as the bare SiO_2 membranes (Fig. 1a). The WN films had a sheet resistance of about 17 kΩ/□.

The TEM of Cu/WN showed discrete, separate crystallites of copper (Fig. 1d) with a nucleation density of about 340 per square micrometer.[c] After an average Cu thickness of 1.4 nm was deposited, the sheet resistance (15 kΩ/□) was only slightly reduced from the value due to the WN alone. Thus the isolated copper islands on WN are connected electrically mainly by the tungsten nitride film.

In contrast, Co (100 cycles, 2 nm) deposited on the WN forms a dense, fine-grained crystalline layer (Fig. 1e). The sheet resistance was reduced to 1.4 kΩ/□, showing that the cobalt grains are in good electrical contact with each other. The TEM of Cu/Co/WN showed a very similar dense, nanocrystalline film (Fig. 1f). The Cu (1.4 nm)/Co (2 nm)/WN (3 nm) film had an initial sheet resistance of 1 kΩ/□ demonstrating that this extremely thin copper film is also electrically continuous. All of these coatings showed increases in resistance between 20 and 60% after oxidation in the ambient air (Table I).

AFM images (Fig. 2 and 3) confirm the conclusions from the TEM images. The amorphous WN films (Fig. 2c and 3c) are just as smooth (rms roughness 0.4 nm) as the Si_3N_4 substrates (rms roughness 0.3 nm, Fig. 2a and 3a). The isolated Cu islands on WN are clearly seen (Fig. 2d and 3d). The nucleation density Cu/WN in the AFM images (Fig. 2d and 3d) is about 300 per square micrometer, slightly less than the TEM value (340), because some of the Cu crystallites are too close together for the AFM tip to resolve. The Cu islands on Si_3N_4 (Fig. 2b and 3b) are seen by AFM, but their edges are not as clearly defined as in the TEM image (Fig. 1b). The fine-grained Co and Cu/Co crystallites can be seen in the AFM images (Fig. 2e and f and 3e and f). The crystallinity of the copper grains was confirmed by high-resolution TEM (not shown), and by X-ray diffraction of thicker (15 nm) copper films (Fig. 4). The dramatic way that cobalt increases the nucleation density of copper is shown by comparison of the rough (rms roughness 5.5 nm) Cu crystallites

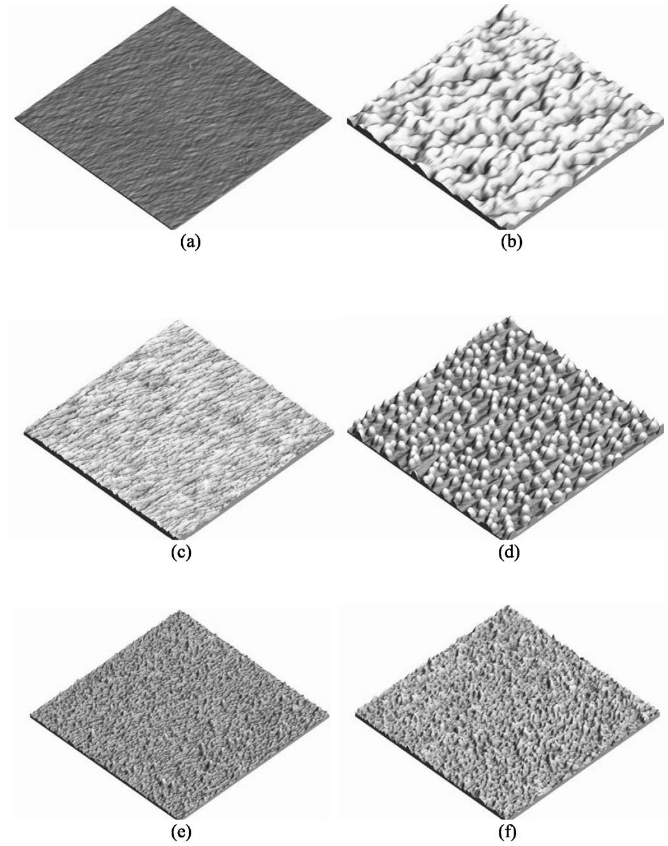

Figure 3. Oblique view of AFM images. (Lettering as in Fig. 1). These images were produced with the software package WS × M©, available by download from http://www.nanotec.es

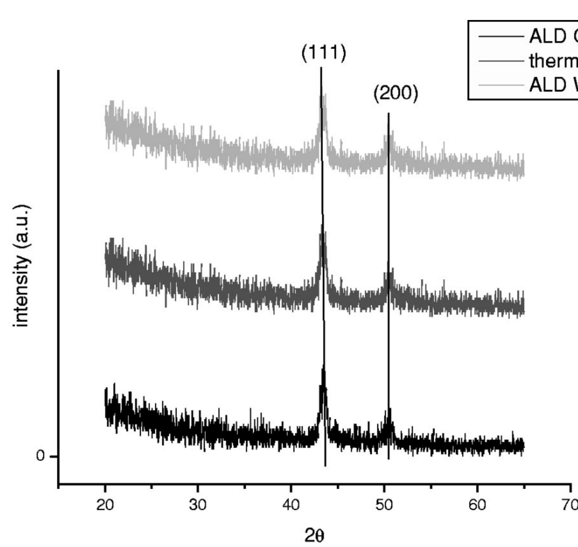

Figure 4. ALD Cu on different substrates at 185°C (0.02 θ stepwise). FCC Cu JCPDS card no. 04-0836.

[c] Because of its high step coverage, ALD coated both sides of the TEM grid, so the nucleation density is one-half of the density observed on the TEM image.

Table II. Adhesion measurements for ALD multilayer structures. Adhesion energy was evaluated by four-point bend tests.

Structure	Scotch tape test	Adhesion energy (J/m^2)
Co/SiO_2	Failed	
Cu/SiO_2	Failed	2[a]
$Cu/WN/SiO_2$	Failed	
TaN/SiO_2	Passed	6[a]
WN/SiO_2	Passed	>31
$Co/WN/SiO_2$	Passed	>31
$Cu/Co/WN/SiO_2$	Passed	>31

[a] Ref. 17.

on WN (Fig. 2d and 3d) with the much smoother (rms roughness 1.6 nm) closely spaced, fine grains of Cu on Co/WN (Fig. 2f and 3f).

Adhesion energies are tabulated in Table II. Co/SiO_2, Cu/SiO_2, and Cu/WN interfaces were easily separated by Scotch tape, resulting in shiny silver- or copper-colored films adhering to the tape. Because of the obviously low adhesion energies of these interfaces, four-point bend tests were not carried out on these samples. A recent four-point bend test[17] on Cu/SiO_2 found rather low adhesion energy of only 2 J/m^2, in qualitative agreement with our results (Table II).

The $Cu/Co/WN/SiO_2$ stack exhibited such strong adhesion that failure occurred at the Si/epoxy interface, rather than at any of the $Cu/Co/WN/SiO_2$ interfaces. This indicates that every one of these interfaces maintained adhesion energy greater than 31 J/m^2, the measured adhesion energy of the Si/epoxy interface. The position of the adhesive failure was confirmed by XPS and RBS analysis of both surfaces exposed by the crack. These adhesion measurements were replicated on at least six separate samples, with a standard deviation around 10%. For comparison, we note that the adhesion energy of WN/SiO_2 is more than five times higher than that of the industry standard TaN/SiO_2. It also surpasses by far Intel's criterion of >5 J/m^2 for acceptable adhesion.[18] It should be noted that if some oxidation of the Co was allowed prior to the Cu deposition, the adhesion energy of the Co/Cu interface was reduced to 6.2 ± 0.7 J/m^2.

We conclude that ALD of Cu/Co/WN can provide a highly conformal, continuous, and strongly adherent seed layers that are suitable for subsequent electrodeposition of copper interconnections for microelectronics.

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