Atomic Layer Deposition of Nickel by the Reduction of Preformed Nickel Oxide

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A thin film of elementary nickel was formed by atomic layer deposition (ALD). The deposition cycle consisted of two consecutive chemical reaction steps: an oxidizing step and a reducing step. An atomic layer of nickel oxide was made by sequentially supplying bis(cyclopentadienyl)-nickel as a nickel precursor and water as an oxidation agent; the preformed atomic layer of nickel oxide was then reduced to elementary nickel metal by exposure to hydrogen radical at a deposition temperature of 165°C. Auger electron spectroscopy analysis detected negligible oxygen content in the grown films, indicating that the hydrogen radical had completely reduced the nickel oxide to a metallic thin film. In addition, carbon impurities in the film dropped from 16 atom % to less than 5 atom % during the reduction reaction. The proposed two-step ALD method for elementary metals was successful in forming continuous and conformal nickel thin films. These nickel films formed an effective glue layer between chemical vapor deposited copper and a diffusion barrier layer of TiN. The adhesion of a 1 μm thick copper film to a 15 nm thick nickel glue layer over a TiN barrier film was excellent, with no failures occurring during adhesive tape peel tests.

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Signal delays and electromigration failures at interconnects are important problems for future integrated devices. Copper, which has both a lower electroresistivity and a higher electromigration resistance than aluminum, is expected to be widely used as an alternative material for future interconnection lines. Copper can be deposited using several techniques, including physical vapor deposition (PVD), chemical vapor deposition (CVD), and electroplating (EP). PVD is an inadequate method of copper deposition due to its inherent inability to deposit conformal thin films on scaled-down holes and trench lines. As an alternative, CVD of copper has been widely investigated, but has the disadvantage of poor adhesion to diffusion barrier metals. To address this issue, we performed atomic layer deposition (ALD) of nickel thin films. Nickel was selected as a glue layer, since nickel and copper form a complete solid solution. Many researchers have examined CVD of nickel using hydrogen gas. These CVD nickel layers were unsuitable as glue layers because they had large grains, with a minimum 20 nm grain diameter, and continuous films could be obtained only for thicknesses of at least 300 nm, which was too thick for the intended use.5 Also, these CVD nickel layers were unsuitable because CVD deposited films would eventually meet application limits in forming conformal films in high-aspect-ratio structures. In this respect, ALD represents an attractive candidate for forming thin and continuous thin films. In ALD, reactants are supplied alternately into the reactor. The non-overlapping alternate injection of the reaction gases prohibits the reaction gases from reacting in the gas phase and thus leads to a deposition that highly depends on adsorption and surface reaction kinetics. The chemical reactions on the wafer surface make ALD a self-limiting process inherently capable of achieving precise monolayer growth.

Recently, ALD of elementary metals, such as copper, titanium, and tantalum, has been reported by Martensson and Carlsson2 and Solanki and Pathangey3 using Cu(I)-2,2,6,6-tetramethyl-3,5-heptanedionato [Cu(thd)2] and copper(I)-1,1,1,5,5,5-hexafluoroacetylacetone [Cu(fhac)2], respectively, as copper precursors, and by Rossnagel4 using TiCl4 for Ti and TaCl5 for Ta. Most of these studies performed elementary metal ALD by reducing the metal precursors directly with hydrogen or hydrogen radicals. ALD of elementary metal by other than direct reduction was reported by Utriainen et al. for nickel deposition.5 NO films were formed by ALD, and then the deposited nickel oxide films were converted to metallic nickel film by heat-treatment at 230°C in 5/95% H2/Ar atmosphere. But the reduction step induced structural collapse, thus pinhole formation was discovered by atomic force microscopic (AFM) images.

In this paper, we demonstrate that nickel thin films can also be formed through ALD using a deposition cycle consisting of two consecutive chemical reaction steps: an oxidizing and a reducing step. ALD of nickel thin films was carried out on TiN (15 nm)/SiO2 (100 nm)/Si wafers at a deposition temperature and pressure of 165°C and 400 Pa (3 Torr), respectively, in a cold-walled reactor. Solid bis(cyclopentadieny)nickel [nickelocene or Ni(cp)2] was used as a metallorganic (MO) nickel precursor; it was held in a stainless steel container heated to 50°C and carried by 100 sccm of argon gas. One cycle of nickel ALD consisted of two consecutive chemical reaction steps. First, the nickel precursor adsorbed on the film surface was decomposed and oxidized by water vapor; then, the atomic layer of nickel oxide formed in the previous step was reduced to metal by hydrogen radicals. The oxidizing step consisted of exposure to Ni(cp)2 vapor, an argon purge period, water vapor exposure, and another argon purge, while the reducing step consisted of exposure to the hydrogen radical followed by a final argon purge. An argon flush was inserted between each reactant gas pulse to isolate the reactants from each other. To ignite the reaction and keep the hydrogen radical synchronized with the deposition cycle, a rectangular-shaped electrical power wave was applied between the upper and lower electrodes. To maintain a uniform gas distribution, a showerhead was used as the upper electrode; it was capacitively coupled with a radio-frequency (rf, 13.56 MHz) radical source and operated at powers of 150 and 50 W. The lower electrode, on which the wafer resides, was grounded. Film thickness was analyzed by transmission electron microscopy (TEM), and the film morphology and step coverage were analyzed by field-emission scanning electron microscopy (FESEM). The film composition was measured using Auger electron spectroscopy (AES), while the chemical state was measured using X-ray photoelectron spectroscopy (XPS).

Preliminary experiments attempted to reduce the nickel precursor directly with the hydrogen radical. All deposition conditions were the same as the nickel deposition conditions, except there was no water vapor exposure. After 200 deposition cycles with Ni(cp)2 and hydrogen radicals only, no metallic film formed on the substrate, except for some particles that could be rubbed off. This suggests that the hydrogen radical by itself cannot completely decompose the MO...
precursor of nickel, Ni(cp)₂, and is unable to easily generate volatile hydrocarbon compounds from cyclopentadienyl to leave elemental nickel on the film surface.

An approach was devised to replace the direct reduction of a nickel precursor by a hydrogen radical. In this investigation, the MO precursor was first oxidized by water vapor, one of the most chemically active oxidants, to remove cyclopentadienyl from the nickel precursor. The nickel oxides thus formed were then reduced into elementary nickel by hydrogen radicals. To generate the hydrogen radical, plasma power was set at 150 W. To confirm whether water vapor can remove cyclopentadienyl and make nickel oxides, ALD of nickel oxides was performed using Ni(cp)₂ and water, and the hydrogen radical step was excluded. After 200 cycles of nickel oxide ALD, dark, deep-blue thin films were deposited. AES analysis showed that the deposited films contained 71 atom % nickel, 13 atom % oxygen, and 16 atom % carbon; XPS analysis showed that the films were composed of a mixture of elementary nickel and NiO. This proved that the nickel precursor reacts with water vapor at a deposition temperature of 165°C, although many carbon and oxygen impurities still remain in the grown film.

As already described, each nickel ALD cycle consisted of the sequential injection of Ni(cp)₂ vapor/argon purge/water vapor/argon purge/hydrogen radical/argon purge. The initial experimental results showed that an elementary nickel metal thin film was deposited by ALD using two consecutive chemical steps.

After 80 cycles of nickel ALD, a thin, continuous nickel film was deposited. Figure 1 shows a cross-sectional TEM image of one of these films. The nickel was polycrystalline, and although it was only about 15 nm thick, it was continuous. This can be compared favorably to the minimum 300 nm thickness necessary to obtain a continuous nickel layer through conventional CVD, which creates a large grain size. The ALD produced film has continuity with a far thinner film than the CVD produced film.

Figure 2 shows a cross-sectional SEM image of a nickel thin film showing excellent conformality over high-aspect-ratio holes. This nickel thin film was deposited on sputtered TaN, which has holes 0.3 μm in diam and 1 μm deep. As expected from the inherent ability of ALD, the nickel films grown by this method showed excellent step coverage and no variation dependent on growth position, such as on the bottom or sidewall of the holes or the substrate field surface.

The oxygen and carbon impurity levels in the films were measured on films thicker (~40 nm) than those deposited under normal conditions to eliminate any effects of the underlying TiN layer. Figure 3 illustrates the AES spectrum of the deposited film after a slight sputtering surface of the film was deposited with an rf power of 150 W. The peak-to-peak values of carbon and oxygen were very low, indicating small impurity levels. The effect of rf power on impurity concentrations in the nickel thin film was investigated. Table I shows AES results of carbon and oxygen impurities in nickel thin films with rf powers of 50 and 150 W. As the rf power increased, the carbon concentration in the thin films decreased from 18 to 5 atom %. Ni(cp)₂ gives high levels of carbon impurities in the CVD processes, with from 3-5 up to 16 atom % carbon incorporated due to easy reactions between absorbed neighboring precursors. Unfortunately, a carbon concentration of 5 atom % is generally too high, since so much carbon may affect the electrical properties of the

<table>
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<th>Plasma power (W)</th>
<th>Carbon (atom %)</th>
<th>Oxygen (atom %)</th>
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<tr>
<td>50</td>
<td>18.7</td>
<td>2.0</td>
</tr>
<tr>
<td>150</td>
<td>5.7</td>
<td>1.9</td>
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Figure 1. Cross-sectional TEM image of TiN, nickel, and copper thin film grown on SiO₂ substrate. The nickel thin films are continuous although they are about 15 nm thick.

Figure 2. Cross-sectional SEM image of nickel thin film grown by ALD at 165°C on sputtered TaN. The film is thick at top of the pattern because the sputtered TaN is not conformal, but the nickel thin film is conformal anywhere.

Figure 3. AES spectrum of nickel film after ALD with Ni(cp)₂, water vapor, and hydrogen radical at substrate temperature of 165°C, pressure of 400 Pa.
nickel thin film, although these were optimum deposition conditions otherwise. The resistivity of 15 nm thick thin films was between 25 and 30 $\mu\Omega$ cm. Since the resistivity of bulk nickel is 6.84 $\mu\Omega$ cm, the higher resistivities in the films were deemed to be due to surface scattering effects and the excessive carbon content. There was a very low oxygen concentration in the deposited thin film, regardless of the rf power used, and the peak-to-peak value for oxygen shown by the AES was negligible in both cases. These results indicate that supplying Ni(cp)$_2$, water, and hydrogen radicals sequentially can make oxygen-free metallic nickel films with small levels of carbon impurities. The hydrogen radical sharply reduced the levels of both carbon and oxygen contaminants.

To test the glue layer ability of the nickel thin film, the adhesion of copper to it was tested using the adhesive tape peel test. After ALD of nickel thin films, 1 $\mu$m thick CVD copper thin films were deposited without a break in the vacuum. The copper films deposited on the nickel layer did not peel off in the test; the nickel glue layer sandwiched between the copper and TiN barrier metal greatly improved the adhesion between the layers.

To summarize, ALD nickel thin films for use as copper layer glues were deposited. It was demonstrated that nickel thin films can be formed by the ALD method using a deposition cycle consisting of two consecutive chemical reaction steps: an oxidizing step and a reducing step. In the oxidizing step, the nickel precursor reacts with water vapor, leaving high levels of carbon and oxygen impurities in the grown film, while in the reducing step, the hydrogen radical removes most of these impurities from the film and leaves polycrystalline metallic nickel.

The deposited nickel thin films were continuous, although the thickness of the film was only about 15 nm. This continuous layer was far thinner than that of conventional CVD nickel. The deposited nickel thin films showed excellent conformality over high-aspect-ratio holes. The adhesion test indicated that the nickel glue layer gave perfect adhesion between a 1 $\mu$m thick CVD copper layer and TiN barrier metal. This newly developed technique, two-step ALD for elementary metal deposition, may be expanded to process other elementary metals.

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