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Utilization of Atmospheric Plasma Surface Preparation To Improve Copper Plating Processes.

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Abstract

Many process steps in semiconductor manufacturing and packaging benefit from pristine surface preparation, such as descuming of photoresist, removal of native oxides, and surface activation. One particularly important surface process is the preparation of surfaces prior to copper plating. New technologies such as Copper Pillar and TSV plating for micron-scale interconnects are particularly challenging. Oxygen ashing is traditionally used to descum photoresist residues in the bottom of a developed-out resist pattern. However, ashing has several disadvantages: 1) it grows additional oxide on the thin layer of copper plating base, 2) changes linewidths in the photoresist pattern, 3) leaves the photoresist surface hydrophobic, and 4) requires the use of a vacuum system.

We demonstrate a new method using Atmospheric Plasma with reducing gas chemistry to provide simultaneously: 1) descuming of photoresist residue, 2) removal of oxidation from plating base, 3) hydrophilic activation of photoresist for instantaneous wetting down into small photoresist apertures, 4) optional passivation of de-oxidized plating base against re-oxidation. All of this is accomplished in room-ambient conditions, eliminating the need for a vacuum system. The need for pre-wetting of the wafers, prior to plating, is also eliminated.

We describe the Atmospheric Plasma apparatus and process used in this alternative method, and demonstrate the benefits of the new technique.

Description of the Atmospheric Plasma System

Figure 1 shows a schematic cross-section of the Ontos Atmospheric Plasma head. Process gas enters at the top of the head, passes through a plasma zone created by an RF field between two electrodes, and exits the head immediately above the target substrate.

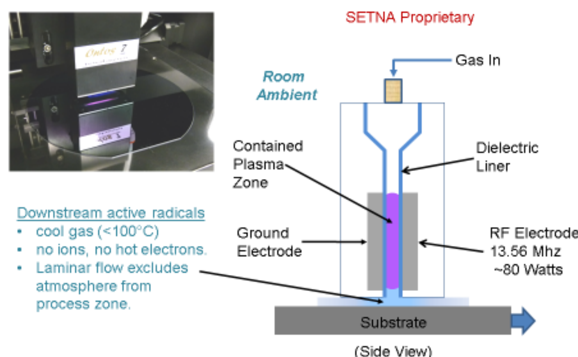

Figure 1. Atmospheric plasma head cross-section

The highly-energetic species of the plasma (ions, hot electrons) are confined within the plasma head and have such a short lifetime at atmospheric pressure that they are re-combined within a few micro-meters of exiting the plasma zone. Chemical radicals, however, have much longer lifetimes and are still active when they contact the substrate below. These chemical radicals may include hydrogen atoms (H*), oxygen atoms (O*), nitrogen atoms (N*), or others. These are highly reactive species ready to chemically react with the substrate surface. Additionally, the downstream gas flow contains metastable helium atoms; which provide approximately 20eV of quantum energy directly to the substrate surface. This energy helps to activate chemical reactions, for example, two H* atoms reacting with an oxygen atom attached to the surface (i.e. a metal oxide) to remove the oxygen from the metal atom, as shown schematically in Figure 2.

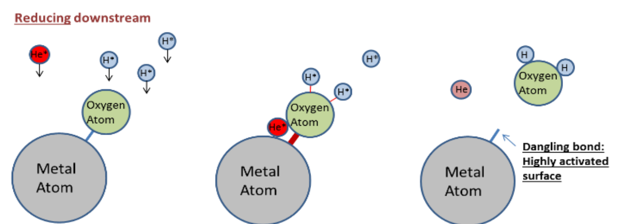

Figure 2. Removal of surface oxygen by atmospheric plasma.

Similar reactions are used to remove carbon, OH, and other contaminants from the substrate surface. Additionally, N* from the upstream plasma can occupy the dangling bonds created by the loss of contaminants, and thereby protect the surface against re-accumulation of contaminants.

The flow of downstream gas from the atmospheric plasma head sweeps all room air from the reaction region at the substrate surface, as seen in Figure 1. This serves a similar purpose as a vacuum system without the need for vacuum chambers, pumping equipment and long pump down times. Therefore, Atmospheric Plasma is very fast and efficient, at a lower cost than vacuum plasma systems. Also, the Atmospheric Plasma head can be positioned above moving conveyors to support continuous feed of substrates, thus eliminating "batch" processing required by vacuum plasma systems.

Descum of photoresist residue

It is broadly recognized in semiconductor processing that there exists a slight residue of photoresist material

(referred to as "scum") in the bottom of a developed-out resist pattern. Oxygen ashing in a vacuum system is typically used to remove this scum [1]. Ontos takes a different direction by using reducing chemistry (i.e. hydrogen-based excited species) to remove post-develop photoresist scum, while having the advantage that any existing oxide on the surface of the exposed plating base is reduced, instead of growing more oxide as would occur with Oxygen-based descuming processes.

To demonstrate this process, a SiO_2-coated silicon wafer was over-coated with a very dilute solution of positive photoresist (AZ4620) in acetone, and then dried on a hotplate. Ellipsometer readings (Figure 3) indicate the presence of approximately 45 Angstroms of AZ4620 residue on the surface. This residue was removed with one to two scans of reducing chemistry by downstream products of atmospheric plasma.

Thus, photoresist residue is removed from the wafer surface. This removal is a highly controlled process which removes only around a hundred angstroms of photoresist, therefore, not affecting PR linewidths significantly.

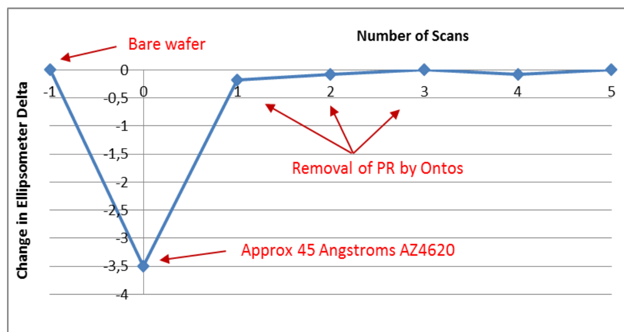

Figure 3: Removal of AZ4620 photoresist residue by downstream reducing chemistry ($He/H_2/N_2$).

Removal of oxidation from plating base

A thin layer of copper is most often used as a plating base (seed layer) as a first step in copper plating for semiconductor manufacturing. Copper oxidizes, when exposed to the atmosphere, growing a layer of CuO/Cu_2O on the exposed surface [2]. The presence of an oxide inhibits the passage of electrical current through the plating base to the plating solution. This oxidation results in variable nucleation of plating onto the plating base, and therefore undesirable non-uniformities in plating thickness. Traditional descuming of photoresist with oxygen serves only to increase the thickness of this oxidation layer. The Atmospheric Plasma with reducing chemistry (i.e. Hydrogen-based excited species) is capable to remove oxidation from the plating base.

The plot (figure 4) shows the removal of copper oxide, using the same $He/H_2/N_2$ parameters as the descum plot, previous. Ellipsometer readings indicate removal of about 60 Angstroms of native copper oxide in one to two scans of the atmospheric plasma. Thus, PR residue removal and plating base de-oxidation can be accomplished during the same process step.

A plating base of nickel responds in a very similar manner.

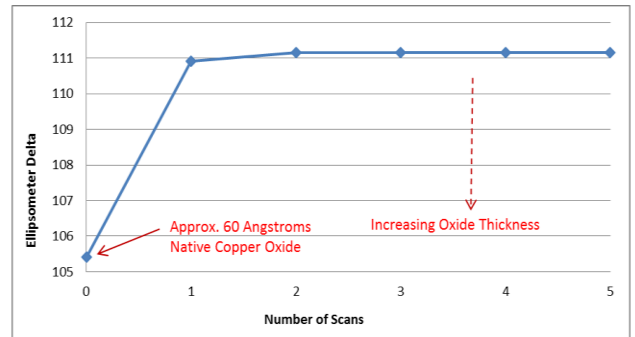

Figure 4: Removal of Copper Oxide by downstream reducing chemistry ($He/H_2/N_2$).

Activation of photoresist for Wetting

Photoresist resin is naturally highly hydrophobic. Small photoresist apertures are notorious for inhibiting flow of aqueous solutions into high-aspect-ratio photoresist patterns, because of this hydrophobic behaviour [3]. Surfactant wetting agents are sometimes added to plating solutions or pre-plating treatments to improve wetting, but these surfactants can create undesirable effects on the plating solutions and subsequent plating quality. Atmospheric Plasma treatment activates the photoresist surface for excellent wetting without compromising plating chemistry.

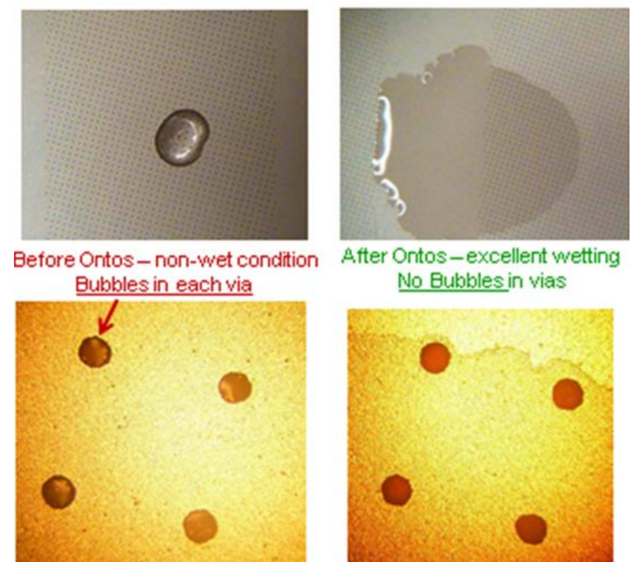

Figure 5: Activation of photoresist pattern to allow wetting of aqueous solution down into high-aspect photoresist via.

In figure 5, the left side shows high-aspect-ratio apertures in a photoresist pattern, imbued with a drop of aqueous solution. The upper left photo demonstrates the poor wetting of the solution to the photoresist layer, on a macro scale. In the lower left, at higher magnification, bubbles can be observed at the top of each aperture, indicating that the solution was not wetting the photoresist well enough to flow down into the small apertures.

In contrast, the right side photos show the wetting of the photoresist on a macro scale, and wetting down into the small via (no bubbles) produced by the application of downstream reducing chemistry from an atmospheric

plasma source. The downstream process parameters which produced this effect were the same $He/H_2/N_2$ as used in the previous two sections of this paper. Thus, PR residue removal and plating base de-oxidation and photoresist wetting can be accomplished during the same Atmospheric Plasma process step.

Optional passivation of de-oxidized plating base against re-oxidation by N_2

The above three advantages could just as well be accomplished without the presence of nitrogen radicals in the downstream. However, with the addition of N* in the downstream from the atmospheric plasma, the de-oxidized copper plating base can be passivated to inhibit re-oxidation of the copper with exposure to air.

Figure 6 shows the re-oxidation of copper as a function of time for three different conditions: a) Fresh clean copper with no surface treatment; b) Copper treated with He/H_2 only; c) Copper treated with $He/H_2/N_2$.

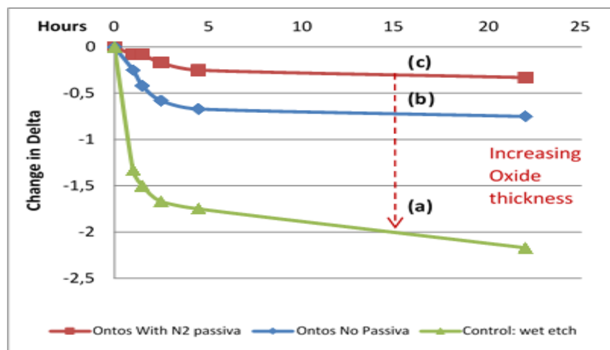

Figure 6: Comparison of Copper Re-oxidation at room temperature

The decrease in Delta value of less than ½ degree over 22 hours signifies a regrowth of only one monolayer of oxide/carbon on the surface. Untreated freshly exposed copper has grown approximately seven times this amount over the same 22-hour period in room ambient conditions.

Thus, the addition of nitrogen to the atmospheric plasma stream prevents thick oxide regrowth on the plating base surface and enables rapid plating initiation on the plating base at very low initial voltage. This provides improved uniformity of plating deposition and decreases the tendency of hydrogen evolution during the plating initiation process.

Optional passivation of activated surfaces by exposure to H_2O

Although the addition of nitrogen adequately passivates the plating base against re-oxidation, the surface activation of the copper and photoresist eventually succumb to airborne oxygen and carbon thus losing their polarity and surface wetting capability. This can be characterized by the formation of more and more bubbles in the bottom of fine geometries. If, however, the substrate is treated with H_2O after the downstream surface treatment described above, H_2O molecules will bind to the activated polar surface and remain as a physisorbed polar monolayer on the surface, even after nitrogen blow-off of excess H_2O. These physisorbed water molecules are stable in air and will remain on the surface for many hours. Their presence inhibits the attachment of oxygen or carbon to the substrate surface. Even days later, this layer of water molecules remains attractive to aqueous solutions and enables exceptional wetting on all surfaces.

Figure 7, shows comparative photographs of three wetting characteristics.

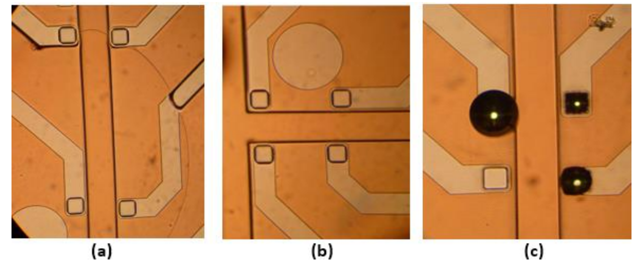

Figure 7: Wetting characteristics comparison

Photo (a) shows the wetting capability of both photoresist and Copper plating base immediately after downstream treatment as described. No bubbles are present due to the exceptional wetting properties of the as-treated surfaces.

Photo (b) shows the same wafer 24 hours later after being re-introduced to an aqueous solution; no bubbles are present because the wetting properties of the surfaces was preserved by the first water exposure.

Photo (c) received downstream treatment, but was left in air for 24 hours (no H_2O treatment). Upon introduction to aqueous solution 24 hours later, bubbles are seen in the geometries indicating that the surfaces have lost much of their wetting properties.

Conclusions

We have demonstrated that Atmospheric Plasma provides a rapid and effective surface treatment which enhances subsequent plating processes. No vacuum system is required, thus enabling continuous throughput. With a single surface treatment process, we achieve: 1) descum of the photoresist pattern, 2) reduction of oxidation on the exposed plating base layer, 3) passivation of the plating base to inhibit oxide regrowth, and 4) activation of the photoresist surfaces to provide thorough wetting even in high-aspect-ratio features. Additionally, we have disclosed the use of an H_2O dip to stabilize the activated surfaces for many hours.

Acknowledgments

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