Initial Stages of Tantalum Nitride Atomic Layer Deposition

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Abstract:

Since the semiconductor industry has moved to porous low-κ dielectrics, thin-film barrier layers to prevent copper diffusion have become increasingly important. In this project, the initial stages of thin-film growth of tantalum nitride deposited via atomic layer deposition were characterized on both low-κ dielectrics and copper, and growth-promoting surface treatments were developed. An ultrathin coating of an interfacial organic layer, polyethyleneimine, increased the growth of tantalum nitride on porous low-κ by reducing diffusion of the precursors and increasing the number of active sites on the surface. Tantalum nitride growth on untreated copper, in contrast, exhibited a long incubation period; while pre-treatments of the surface were found to decrease the incubation time.

Introduction:

As features sizes in integrated circuits approach the nanometer scale, there is an increasing need for highly conformal, precisely-controlled thin film deposition. Atomic layer deposition (ALD) has emerged as an ideal method to deposit a variety of materials used in modern semiconductor devices. Its conformal growth arises out of its layer-by-layer process—precursors are alternately injected and purged from a low-pressure system, which builds up a film, layer by layer. Though it is very useful, many materials remain difficult to deposit via ALD because chemical interactions at the thin film-substrate interface govern the initial stages of nucleation and growth in this deposition process. This project investigated ALD of tantalum nitride (TaN), one of the most attractive materials for diffusion barriers between copper interconnects and the dielectrics that surround them. Growth on both copper and porous low-κ dielectrics was studied, and interfacial organic layers were identified to promote growth in the early stages of ALD. Growth rates and film uniformity were studied using x-ray photoelectron spectroscopy and spectroscopic ellipsometry, while atomic force microscopy was used to characterize the nucleation of the TaN films.

Experimental Procedures:

Atomic layer deposition was carried out at 250°C on an Oxford FlexAL machine using pentakis(dimethylamino)tantalum and ammonia precursors. Industry-supplied porous low-κ and copper wafers were used for all experiments. The polyethyleneimine capping layer was deposited on the porous low-κ wafers with a 15-minute soak in a 0.1% by weight solution of polyethyleneimine in water. Ellipsometry revealed that the thickness of the capping layer was on the order of 3Å. This solution was prepared using polyethyleneimine purchased from commercial suppliers with no further purification.

Results:

Deposition on Porous Low-κ. Angle-resolved x-ray photoelectron spectroscopy and atomic force microscopy (AFM) were used to examine the initial stages of growth of TaN on porous low-κ. As illustrated by angle-resolved

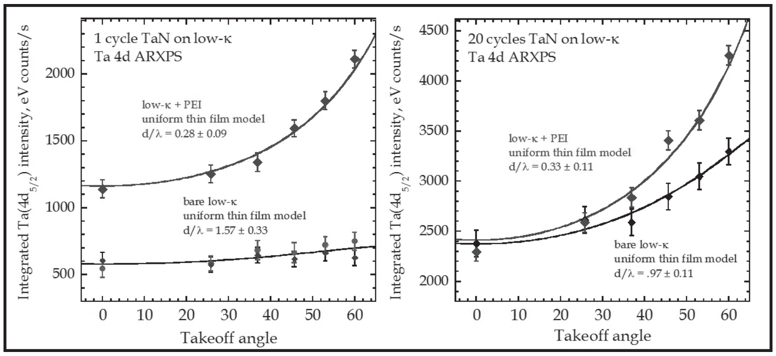

Figure 1: Angle-resolved x-ray photoelectron spectroscopy of the tantalum signal in untreated and porous low-κ treated with an interfacial organic layer at one cycle (left) and 20 cycles (right) of ALD.

x-ray photoelectron spectroscopy results in Figure 1, deposition on untreated porous low-κ resulted in poor growth and TaN diffusion into the dielectric. This diffusion was virtually eliminated by the use of the interfacial organic layer, polyethyleneimine. While the TaN film uniformity on untreated porous low-κ improved by 20 cycles, the low-κ treated with the interfacial organic layer still exhibited superior performance.

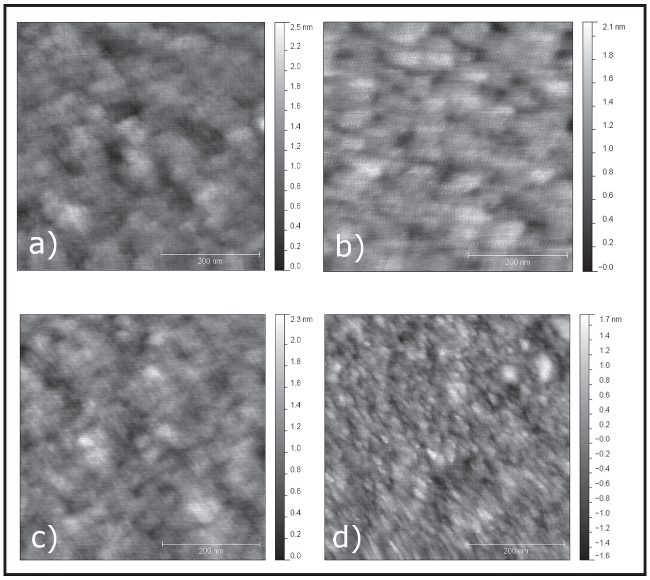

Figure 2: AFM images of; a) untreated porous low-κ before deposition, b) polyethyleneimine-treated porous low-κ before deposition, c) untreated porous low-κ after 20 cycles of TaN deposition, and d) polyethyleneimine-treated porous low-κ after 20 cycles of TaN deposition.

Improvements in growth and nucleation on the polyethyleneimine-treated porous low-κ were confirmed by comparing AFM images of the treated and untreated wafers after a number of cycles. As shown in Figure 2, the treated and untreated porous low-κ are virtually indistinguishable before deposition (2a and 2b), but after 20 cycles of TaN ALD, the TaN film on the treated porous low-κ (2d) shows a developing grain structure, while the untreated porous low-κ still has the cloud-like morphology of the pre-deposition substrates. Unfortunately, since ellipsometry on porous low-κ yielded unreliable results, we were unable to characterize the growth rate per cycle.

Deposition on Copper. As shown by the previous results with the polyethyleneimine-treated porous low-κ, even the first few angstroms (Å) of the surface can heavily influence growth. As such, we hypothesized that the native oxide layer might play a significant role in the deposition of TaN on copper.

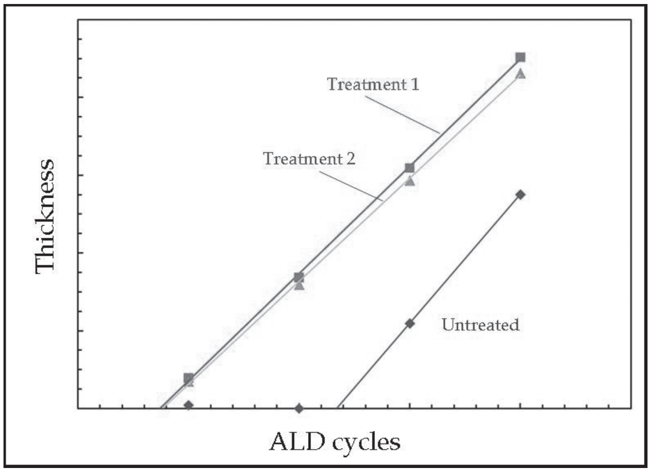

Figure 3: Growth rates and incubation time of untreated, and pretreated copper samples.

To study the possible effects of the state of the starting surface, we measured deposition on untreated copper, and copper exposed to one of two treatments. Figure 3 illustrates the growth rate and incubation time for the three different sets of conditions. As can be seen in the figure, both pretreatments significantly reduce the length of the incubation period. Furthermore, since they have statistically identical effects on the deposition, we propose that the decrease in incubation time was indeed achieved by chemically modifying the state of the starting surface.

Conclusions:

The initial stages of TaN growth by ALD were studied on porous low-κ dielectrics and copper. A polyethyleneimine interfacial organic layer on porous low-κ reduced tantalum diffusion into the dielectric and facilitated uniform growth on the surface. These results were confirmed by angle-resolved x-ray photoelectron spectroscopy and atomic force microscopy. On copper, ellipsometry was used to determine the growth rate and incubation time on untreated surfaces, and surfaces exposed to treatments intended to modify the starting surface. These treatments both significantly reduced the incubation time.

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