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Promixity Effect of Selective Co ALD on the Nanoscale

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***Abstract*— The atomic layer deposition of cobalt using $Co(DAD)_2$ and tertiary-butyl amine (TBA) has nearly infinite selectivity (>1000 cycles) on metal vs. insulator (SiO_2 or low-k SiCOH) planar samples. However, on patterned samples, selectivity under identical ALD conditions is limited, due to the diffusion of molecularly-adsorbed metal precursor from reactive to non-reactive surfaces. Four strategies have been found to improve Co ALD selectivity: adding a passivant to remove insulator defect sites, increasing the purge time, decreasing the precursor dose, and periodic annealing. The periodic annealing technique allows reabsorption of the Co nuclei from the insulator surface to the growth surface and is consistent with a low temperature reflow process.**

Keywords—atomic layer deposition, selective-area ALD, cobalt

I. Introduction

As previously reported, the atomic-layer deposition (ALD) of Co on metals vs insulators such as SiO_2 using bis(1,4-di-tert-butyl-1,3-diazadienyl)cobalt ($Co(DAD)_2$) and tertiary butyl amine (TBA) or formic acid (HCOOH) has nearly infinite selectivity at 180°C (>1000 cycles) due to the formation of CoO_x on insulators, preventing further dissociation of $Co(DAD)_2$ and terminating the reaction. This process is desired as no passivation is required for high selectivity on blanket insulating surfaces [1,2]. Other Co ALD techniques with high selectivity exist, but often require elevated temperatures and co-reactants such as O_2 which are incompatible with low k dielectrics such as SiCOH (methyl-terminated porous SiO_2) used in middle and back-end of line processing (MOL and BEOL) [3]. For MOL and BEOL, selectivity must be maintained on the nanoscale between the metal growth surface and the insulators.

In this report, Co ALD was performed using $Co(DAD)_2$ + TBA at 180°C on 85 nm wide Cu stripes on SiO_2. The planar structure of these stripes is used to demonstrate the effectiveness of passivation, as top-down scanning electron microscopy (SEM) imagery and x-ray photoelectron spectroscopy (XPS) quantification can be used to monitor growth and presence of unwanted Co nuclei on insulator. To control precursor dose, multiple precursor pulses were employed in each cycle to limit the maximum pressure when using a turbomolecular pump which minimizes background oxidants such as H_2O which might contaminate the films and/or impair selectivity. XPS is performed without breaking vacuum to prevent oxidation of Co. Finally, cross-sectional transmission electron microscopy (TEM) of the trenches was also performed.

II. Breakdown of Selectivity on the Nanoscale

The $Co(DAD)_2$ + TBA ALD process was employed on patterned substrates with Cu lines separated by SiO_2. XPS quantification shows Cu attenuation and persistence of Si, consistent with selective deposition, but SEM imaging shows Co nuclei on the non-reactive SiO_2 surface (see Fig 1). The nuclei are at high density near the Cu, tapering off with distance from the stripes. In addition, nearly all the nuclei are of similar diameter. This is consistent with unwanted nuclei being formed by diffusion of the $Co(DAD)_2$ precursor from the Co growth surface on the Cu to SiO_2 where it is converted to Co with a subsequent TBA pulse. On unpatterned SiO_2 surfaces, the observed hyper-selectivity (not shown) is consistent with a lack of molecular adsorption, but it is hypothesized that hydroxyl groups on SiO_2 combined with the proximity of the Co/Cu surfaces may result in unwanted adsorption of Co precursor, and thus, unwanted nucleation.

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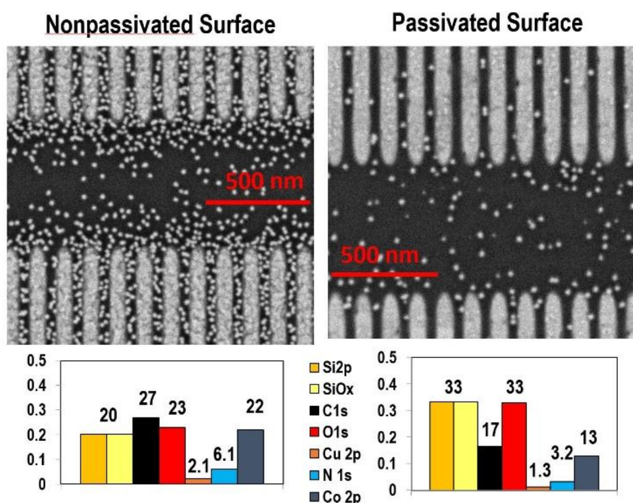

Fig. 1. 200 Cycles of $Co(DAD)_2$ + TBA at 180°C on a Patterned Cu/SiO_2 structure. The Cu stripes are gray and the SiO_2 areas are black. (left) After 200 cycles on the unpassivated sample, unwanted Co nuclei are observed close to the Co/Cu stripes. (right) On a passivated sample, the density of unwanted nuclei is 4x lower and more uniform across SiO_2.

To confirm this hypothesis, the Cu/SiO_2 patterned sample was passivated with vapor-phase dimethylamino-dimethyl-silazane (DMADMS) and tetramethyl-disilazane (TMDS) for 10 minutes at 70°C and 200 cycles Co ALD performed. This molecule is commonly used for SiCOH repair. As shown in Fig. 1, the number of unwanted nuclei is reduced by at least 4x and the uniformity of the nuclei on the SiO_2 increased. This is consistent with the passivation of defect sites on the SiO_2, leaving $Co(DAD)_2$ with a longer surface diffusion path and, therefore, a higher probability to re-adsorb on the metal stripes.

III. Two Methods of Diffusion Control

The $Co(DAD)_2$ + TBA ALD is unusual because XPS data is consistent with molecular instead of dissociative chemisorption of $Co(DAD)_2$ at 180°C because the XPS data shows that the $Co(DAD)_2$ ligands are largely intact after the surface is dosed with $Co(DAD)_2$ (not shown) This implies that the $Co(DAD)_2$ adsorption is reversible; therefore, it was hypothesized that selectivity could also be improved by increasing the purge time, so $Co(DAD)_2$ which diffused onto the SiO_2 can desorb before the pulse of TBA removed the DAD ligands from $Co(DAD)_2$, inducing irreversible adsorption. As shown in Fig 2(a), increasing the purge time from 5 seconds to 30 seconds decreased the density of unwanted nuclei consistent with the $Co(DAD)_2$ diffusion and reversible adsorption hypothesis, but the effect is less drastic than the effect of passivation.

The $Co(DAD)_2$ likely adsorbs strongly to the Co metallic growth surface, but during each ALD cycle, excess $Co(DAD)_2$ is employed to ensure saturation so the growth surface is not metallic Co at the end of the $Co(DAD)_2$ dosing. It was hypothesized that during each cycle once the growth surface was saturated with $Co(DAD)_2$, further $Co(DAD)_2$ dosing would result in diffusion onto the SiO_2. To test this hypothesis,

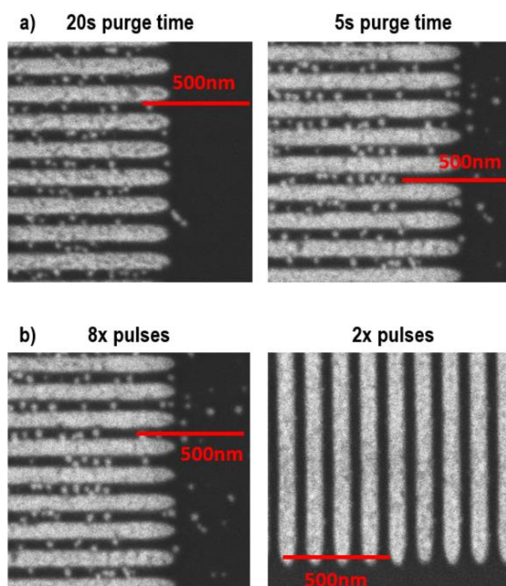

Fig. 2. 200 Cycles of $Co(DAD)_2$ + TBA at 180°C on a Patterned Cu/SiO_2 sample. The Cu stripes are grey and the SiO_2 areas are black. (a) Increasing pump-out time has weak effect on nucleation density. (b) The dose of $Co(DAD)_2$ in each cycle was reduced by 4x. Note the near perfect selectivity, but overall growth rate was reduced 2x.

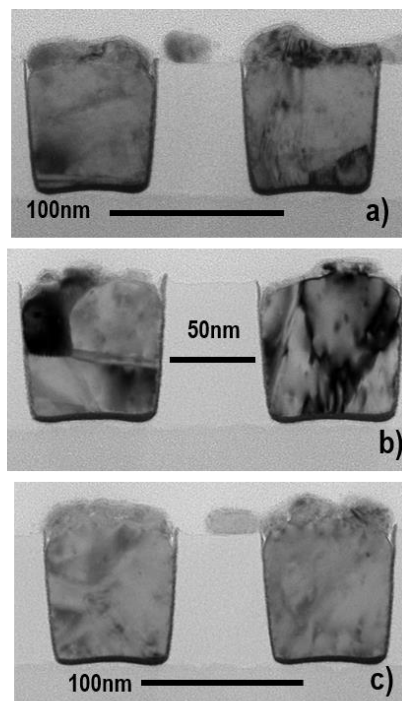

Fig. 3. TEM of 200 Co ALD cycles with varying purge time and dose. The Cu stripes are dark grey and the SiO_2 areas are white. (a) With 8 pulses of Co precursor per cycle, and 5s purge time, unwanted nucleation density is high. (b) Reducing Co pulse count to 2 pulses/cycle lowers the growth rate. (c) Increasing the purge time from 5s to 20s improves unwanted nucleation density, but higher precursor does not eliminate unwanted nucleation.

a lower $Co(DAD)_2$ dose was employed by reducing the number

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of pulses per cycle. As shown in Fig 2(b), this was very effective in reducing the number of unwanted nuclei on the SiO_2, but also reduced the growth rate.

In addition, cross-sectional TEM was performed in Fig. 3, further illustrating the effects of purge time and dose. In Fig. 3(a), unwanted nucleation density on the confined SiO_2 strips is high, consistent with the top-down SEM results. In Fig. 3(b), the thinner layer of Co on Cu is consistent with a lower growth rate, while in Fig. 3(c), the lengthened purge time reduces, but does not eliminate unwanted nucleation. The results confirm the hypothesis that the loss of selectivity on the nanoscale is due to surface precursor diffusion.

IV. Two Methods of Diffusion Control

A third method to improve selectivity was tested: After each 100 Co ALD cycles, an anneal to 260°C was performed; this is about 100°C below the normal Co reflow temperature. However, according to the simple Ostwald ripening model, atoms from small nuclei can more readily diffuse than atoms from large nuclei; therefore, by annealing the sample when the nuclei are small, it may be possible to induce Co diffusion from the nuclei to the Co/Cu stripes. As shown in Fig. 4, periodic annealing resulted in near perfect selectivity on a

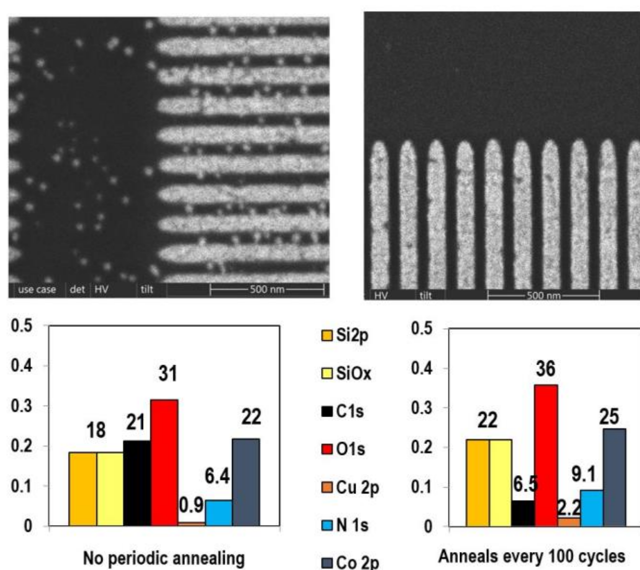

Fig. 4. 200 Cycles of $Co(DAD)_2$ + TBA at 180°C on a Patterned Cu/SiO_2 sample with 260°C Periodic Anneal. The Cu stripes are grey and the SiCOH areas are black. (left) Note the near perfect selectivity. No passivation was employed, only a 5 second pumpout was employed, and saturation $Co(DAD)_2$ doses were employed to get maximum growth rate and conformal deposition.

Cu/SiO_2 pattern without passivation. Fig. 5 shows a cross-sectional TEM of the ALD cycles with and without periodic annealing, with removal of the unwanted nucleation on SiO_2. Furthermore, the formation of a bulge at the edges of the

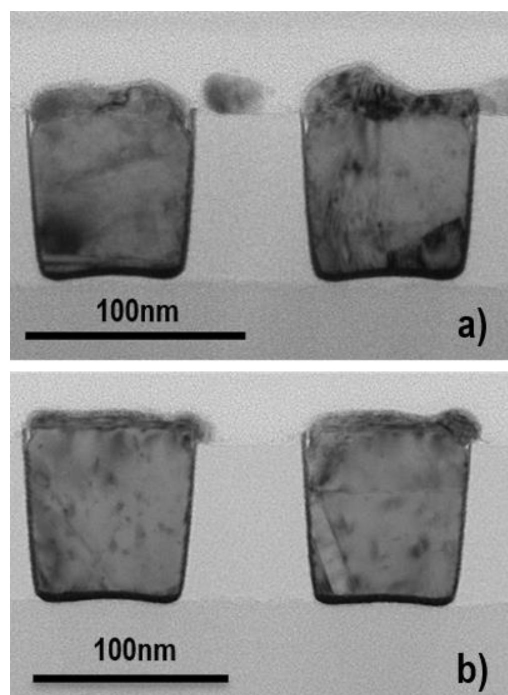

Fig. 5. TEM of 200 Co ALD cycles with and without Periodic Annealing. The Cu stripes are dark grey and the SiO_2 areas are white. (a) Without periodic anneal, unwanted nucleation is observed on SiO_2. (b) After periodic anneals every 100 cycles, a denser film is observed, with formation at edge consistent with nanoscale reflow of Co.

stripes is consistent with the reflow of Co on the SiO_2 to the edges of the Cu growth surface. This technique has the added advantage of allowing a lower temperature for reflow, potentially allowing a scaling of the diffusion barrier between the Co and the SiCOH which is normally employed.

Acknowledgment

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