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Title: *Strategies for selective deposition and selective etching of metal oxide materials on patterned substrates*

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As the sizes of microelectronic devices continue downward scaling, novel processing methods are needed to meet the increasingly difficult materials challenges associated with the new devices. To achieve complex planar geometries and 3-D structures such as FinFETs with nanometer-scale feature sizes, selective deposition processes may help facilitate the fabrication process. Selective deposition approaches in device fabrication require a technique that can provide for deposition of different materials with a variety of thicknesses while maintaining the selectivity up to high thickness limits. Here we describe area selective deposition using a combination of self assembled monolayers (SAMs) and atomic layer deposition (ALD).

ALD is a good choice for selective deposition because it is based on self-limiting reactions between gas phase precursors and specific functional groups at the growth surface. This chemical specificity provides a means to achieve selectivity in ALD on a spatially patterned substrate. Selectivity is obtained by passivation of the surface using SAMs in the regions where deposition is not desired. For selective deposition of metal oxides, we will describe two systems. First, we explore strategies for achieving area selective deposition of dielectric materials by selectively depositing an organic SAM as the blocking layer on metal regions of a metal/dielectric (Cu/SiO₂) substrate pattern. We show that both alkanethiol and alkylphosphonic acid SAMs can prevent subsequent deposition of metal oxide dielectric films via ALD on copper. We also introduce results showing that regeneration of the alkanethiol SAM protecting layer between ALD cycles is effective in improving the blocking properties of the SAM on Cu. This strategy provides the ability to carry out selective deposition for film thicknesses greater than 30 nm, opening up the possibility for new applications in next generation electronic devices. In the second system, we investigate a new approach which allows for both a decrease in the otherwise long deposition time required to form a well-packed phosphonic acid SAM passivation layer and a significant improvement in the deposition selectivity for more reactive dielectric precursors. To this end, we combine selective deposition and selective etching of dielectric films on a metal/dielectric pattern. We first selectively deposit phosphonic acid SAMs on a Cu/SiO₂ pattern at a reduced deposition time. Subsequent ALD of a dielectric material on the substrate results in poor selective deposition. Then a mild etchant is used to selectively remove the deposited dielectric film from the Cu surface without affecting the film deposited on SiO₂. We show that using this method, a high selectivity can be achieved while significantly reducing the processing time for deposition of a variety high-κ dielectric materials.