Effect of Starting Surface in Atomic Layer Deposition

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In the near future the semiconductor industry will need to adopt new materials and materials processing technologies in order to continue down-scaling of device feature size. The down-scaling requires the SiO_2 gate oxide to be replaced with an ultra thin metal oxide with a higher permittivity than that of SiO_2. In the metallization ultra thin Cu barrier and seed layers should be deposited on the dual damascene structure with 100% conformality. Metal oxide and nitride layers with thickness of even less than 30Å are today studied for gate oxides and Cu barriers. It has been shown that the atomic layer deposition (ALD) technique can be applied to the deposition of ultra thin and uniform metal nitride and oxide films on large substrate area. Due to the ultra thin nature of the films the understanding of how the starting surface affects the ALD growth and the materials properties is, therefore, becoming highly crucial. It must also be noted that besides binary materials also various mixed materials, graded layers and nanolaminates are being deposited by ALD through the molecular layer-by-layer growth mechanism, which makes the definition of starting surface for each individual layer not so straightforward.

The initial starting surface in ALD can for instance be the Si wafer surface covered with a thin silicon oxide or nitride layer. During the very first reaction cycles consisting of the metal compound reaction and non-metal compound reaction as well as of the purging step in between the reactions, the surface condition of the growing layer after each reaction cycle is different from that of the previous reaction cycles. Thus, the starting surface changes the entire time until the surface is fully covered and the bulk film growth starts. The number of cycles required to fully cover the surface depends on the initial surface condition and the metal precursor in question. An interesting example is the deposition of nanolaminates consisting of separate layers of different oxides or nitrides. The layers can either be grown so thick that the surface is fully covered and the bulk growth mode starts or they can be grown so thin that bulk growth mode is never reached leading, thus, to continuous change in the starting surface throughout the growth of the ultra thin film. Due to the stepwise nature of the ALD process the surface condition after each reaction cycle can independently be studied, which makes the studies on the ALD growth highly interesting also from fundamental materials growth point of view.

In this paper the effect of starting surface on the ALD growth is presented with a number of examples. The examples are given from both growing of metal oxides like HfO_2, silicates and aluminates and of metal nitrides/carbides like TiN and WN_xC_y. A special emphasis is put on the initial starting surface.