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Atomic-layer-deposited Al₂O₃ as a barrier to thermal and plasma oxidations

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Introduction

Atomic-layer-deposition (ALD) of nanometer-thick layers of Al₂O₃ or other dielectrics has been established to be an effective method to create encapsulation layers of sensitive materials against their degradation by the ambient atmosphere moisture and oxygen content [1,2]. Independently, the corrosive transformation of semiconductor materials into insulators induced by oxygen (respectively water), referred as dry (resp. wet) oxidation, are often used in the fabrication of microelectronic and photonic devices and integrated circuits as a way to introduce the electrical and/or photonic confinement needed to implement the on-wafer optical routing [3–6] and/or electrical connections. In particular, in silicon photonics device fabrication, the latter processes typically involve high temperature or plasma exposure of a silicon layer to water/oxygen with local oxidation protection achieved by SiN_x masks whose thickness is greater than 100 nm [3,4].

In that context, we report here an investigation of the ability of using ALD-deposited Al₂O₃ as a material-sparing oxidation barrier against plasma-induced or high-temperature thermal oxidation of silicon wafers.

Sample Preparation

Al₂O₃ films with nanometric thickness are deposited by thermal ALD on silicon wafers. The low-pressure thermal ALD deposition is composed of repeated cycles, each of which consisting of a 300-ms pulse of trimethylamine aluminum (TMA) successively followed by a 2800-ms purge under N₂, a 150-ms pulse of water vapor, and a second purge under N₂ of 6700 ms. Two deposition temperatures, 90°C and 150°C, are tested here.

The resulting layer thickness is measured using variable-angle spectroscopic ellipsometry (using an Accurion EP4 system). The recorded evolution of the thickness of Al₂O₃ as a function of the number of deposition cycles is shown in Figure 1. At 0 cycle, the measured thickness corresponds to the native silicon oxide (~2 nm measured). Up to 15 deposition cycles, the nucleation starts with a heterogeneous growth (see inset of Fig 1). Beyond 15 cycles, the deposited thickness is found to increase linearly at a growth rate per cycle (GPC) of 0,19 nm/cycle and to be weakly dependent on the deposition temperature.

The Al₂O₃-coated samples are subsequently patterned using UV photolithography and wet etching in order to obtain samples with Al₂O₃-protected and unprotected silicon areas. The layer etching is carried out with diluted phosphoric acid (with DI water/H₃PO₄ (37%) 1/1 solution) at a precise temperature of 67°C, leading to an etching rate of 30 nm/min. Rinsing and cleaning are carried out with water and acetone, respectively.

Two types of oxidation are tested: a dry thermal oxidation and a plasma oxidation. The dry thermal oxidation protocol consists of a linear rise in temperature (8.2°C/min) from 30°C under an O₂ flow of 5L/min, followed by a constant temperature step at 1000°C under an O₂ flow of 9L/min followed by a temperature decay at -16.3°C/min under O₂ flow of 5L/min. The low-pressure O₂ plasma oxidation is carried out in a Sentech Si-500 equipment using repeated 30-min treatments where the samples are subjected to an O₂ plasma, with 800W RF-power and a substrate temperature maintained below 100°C. In both cases, the oxidation thickness in the protected and unprotected zones of the treated samples is measured by imaging spectroscopic ellipsometry. Figure 2. left shows that the dry oxidation does not proceed should the Al₂O₃ be thicker than ~9 nm (45 cycles) and is reduced for thinner capping layers. This observation is further confirmed by the SEM cross-section (shown as an inset in Figure 2). Similarly, the plasma oxidation is observed to lead to an oxide growth that follows a square-root-law time dependence (Deal and Grove model [7]) but whose oxidation rate is reduced for the (30-cycle) Al₂O₃-coated part of the samples.

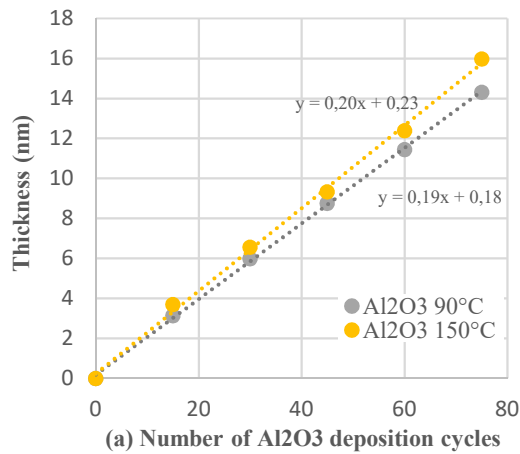


Figure 1. Ellipsometry measurements of the thickness of the Al₂O₃ layers deposited by thermal ALD.

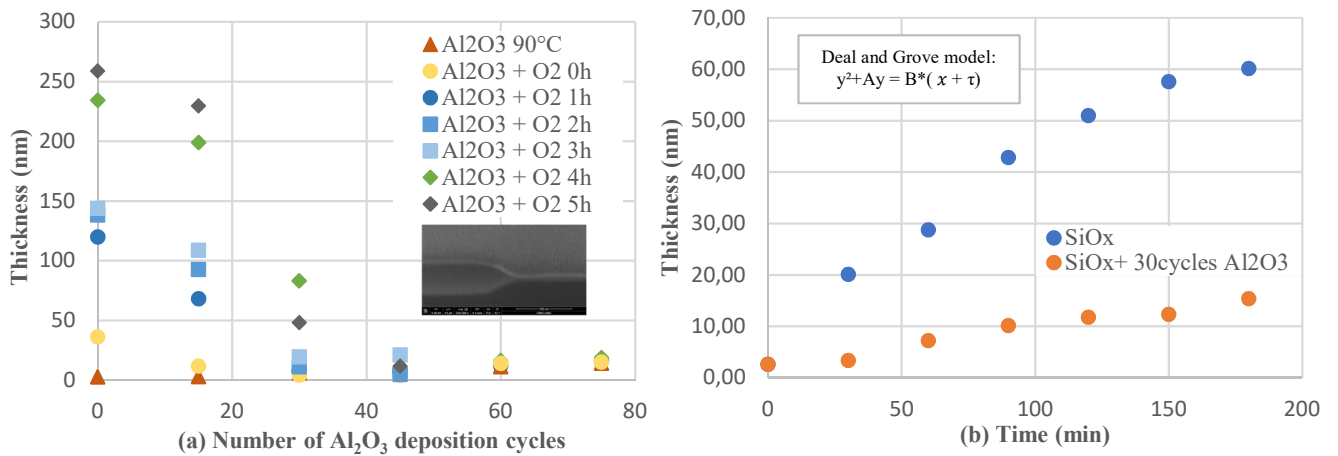


Figure 2. Ellipsometry measurements of (a) the dry thermal oxide thickness (with, as an inset, an SEM image of the oxide at an edge of an Al₂O₃ covered area (right)) and (b) of the plasma-induced oxide.

Conclusion

We have demonstrated that ALD-deposited Al₂O₃ layers can be effective barrier layers to the thermal and plasma oxidation of silicon. Subsequent work will be devoted to use the above-established processes in the fabrication of photonics devices such as microring resonators.

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