Selective Bottom-Up Growth of Organic Film from Cu in Cu/SiO_2 Patterns and Its Usage for Selective ALD as an ALD Inhibitor

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Abstract

This paper reports on the bottom-up growth of organic films only on the Cu surface of a Cu/SiO_2 pattern using a chemical solution developed by TOK. The organic film was formed with a thickness of 100 nm or more at a growth rate of approximately 5 nm/min, although the pattern may collapse depending on the aspect ratio. Furthermore, surface modification of organic film with another solution was evaluated, and 6nm thick ALD inhibition was confirmed under surface passivation. This development could lead for application towards bottom-up growth processes, including as a pretreatment agent for area selective ALD, and it could expand the possibilities for future patterning.

Keywords: Selective deposition, Area selective ALD

Introduction

In recent years, extensive research has been conducted on area-selective ALD, aiming to apply it to a wide range of applications particularly in the semiconductor field such as fully self-aligned vias[1], and selective deposited barrier for advanced interconnect[2]. Approaches to selective ALD can be categorized into different cases: 1) those that utilize the inherent selectivity of precursors[3, 4], 2) those that control processes, such as temperature, pressure, and plasma[5, 6] , and 3) those that form Self Assembled Monolayer (SAM) material with desired selectivity via wet or dry process and passivates the surface prior to the ALD process.[7, 8, 9] In all of the above cases, it is still difficult to form a thick ALD film without overhang. One of the proposed solutions is to form an ALD-inhibiting layer with a thickness exceeding that of a monolayer. In the past, studies have been conducted involving the selective formation of polymer films prior to ALD; however, a challenge associated with this approach was that the polymer itself tended to overhang and cause exclusion[10]. The cause of the selective ALD with polymer is typically adsorption selectivity of the polymer's terminal functional groups. With the aim of addressing the challenges describing above, this study investigated the selective formation of organic polymer through different mechanisms. Specifically, this is a bottom-up and in situ polymer formation technique by utilizing reactions with substrate or catalytic effects of the substrate. In this paper and presentation, we discuss the morphology and growth rate of the formed organic films, as well as their ALD inhibition capabilities with surface passivation.

Experimental Methods

A. Pattern Wafer: The post-CMP wafers used in this research were fabricated in collaboration with imec-Leuven. The wafer was cut into coupons of a few centimeters in size for evaluation. All evaluations were performed on 50nm/50nm Cu/SiO2 patterns with a Co liner. The Cu thickness is 40nm.
B. Blanket wafer: The blanket Cu and SiO_2 wafer were used for this research. The stack of the Cu blanket is Cu 30nm / Ta 20nm / Si. Cu and TaN were deposited with sputtering. SiO_2 was thermally formed on Si with 100nm thickness.
C. Treatment method: The coupon was first dipped in 25 ppm dHF aqueous solution at room temperature for 1 minute to remove contamination from the environment. Next it was dipped in 0.5% citric acid aqueous solution at room temperature for 1 minute to form a Cu oxide film. Then it was dipped in a 60°C TOK solution A, rinsed with IPA, and dried with N_2 blow. For some evaluation, the coupon was dipped in TOK solution B additionally to terminate the surface with different functional groups, and it was rinsed with IPA and dried with N_2 blow. The temperature and dipping time for TOK solution B was 60°C for 2min. After dHF and citric acid treatment, the coupons were rinsed with water and dried with N_2 blowing to avoid mixing of the chemical solutions.
D. SEM observation: After the chemical treatment, the coupon was cut and Pt was deposited by sputtering (Hitachi's MC-1000 /15mA-15s). The cross section was observed using SEM (Hitachi's SU-8000).
E. ALD evaluation: To evaluate the ALD inhibition effect, TiO_2 was deposited at 80°C using AT-400 from Anric Technology. TDMATi was used as the Ti precursor, and H_2O was used as the oxygen source. The thickness of the deposited TiO_2 film was measured using XRF ZSC Prius IV from Rigaku.

Results and Discussion

A. Organic film formation: The coupons were treated under the conditions described in the Methods section, and the cross section was observed using an SEM. Figure 1 shows the progress of organic film growth with dipping time. An organic film grew on the Cu longer as the dipping time increased. On the other hand, no organic film was formed on SiO_2, confirming the selectivity of the film formation. The shape of the organic film was a vertical structure relative to the pattern, which is due to the bottom-up deposition. Therefore, the tip of the film does not grow by reaction with new molecules but rather a reaction at the interface on Cu, causing the film to accumulate and rise, resulting in this vertical shape. Although the pattern collapsed due to the aspect ratio, it is possible to deposit organic films with thickness over 100 nm.

Figure 2 also shows the relationship between the thickness of an organic film on Cu and the dipping time. The film growth rate is constant and occurs quickly (5 nm/min).

The coupons treated with the same procedure were observed with SEM at tilt angle 20 degrees. Through Figure 3 with the summary of these SEM images, the line edge roughness displays well in the early stages of film formation, especially at 4 minutes and 5 minutes.
B. ALD evaluation: The surface of the organic film formed on Cu can be terminated with different functional groups by using surface termination chemistry. Terminating the surface with a hydrophobic group can passivate the surface and inhibit ALD. TiO_2 was deposited with ALD on a coupon that was only pre-treated with dHF and citric acid. In addition, TiO_2 was also deposited on another coupon after treated with dHF, citric acid, TOK solution A to form an organic film (dipping time: 5min), and TOK solution B for the surface to passivate. Then, the thickness of these deposited TiO_2 films were compared. Figure 4 and Figure 5 reveal the relationship between the number of ALD cycles and the TiO_2 thickness of Cu wafer and SiO_2 wafer. On Cu wafer, 6 nm TiO_2 film was deposited on the coupon treated by only dHF and citric acid after 600 cycles, whereas the coupon treated with the two TOK chemicals displayed only a 0.1 nm film. On SiO_2 wafer, 6nm TiO_2 film was deposited on both coupons. Therefore, 6nm of TiO_2 was selectively deposited on SiO_2 and not on Cu by using 2 types of TOK chemicals.

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* We have filed a patent for this technology.

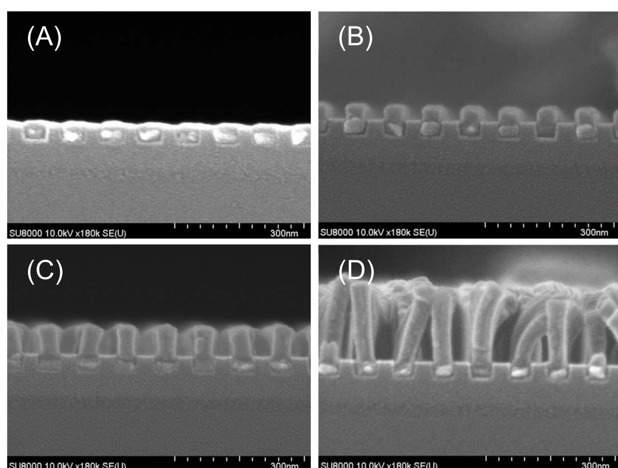

Fig. 1. SEM images for cross section of the coupons treated by TOK chemical at 60deg.C for (A) 1min, (B) 5min, (C) 10min, (D) 30min.

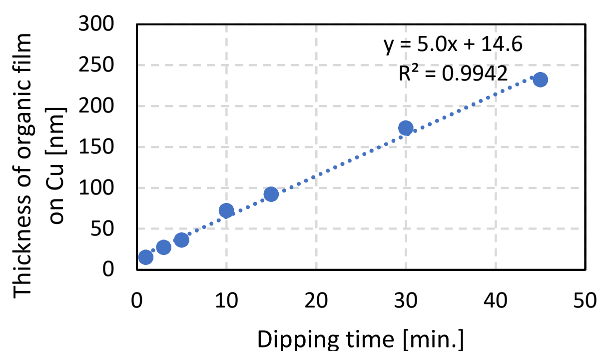

Fig. 2. The relationship between the thickness of an organic film on Cu and the dipping time of TOK chemical.

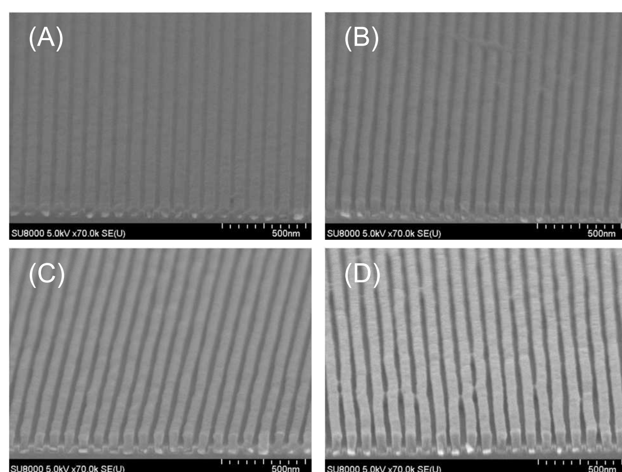

Fig. 3. SEM images for cross section at tilt angle 20degree. These coupons were treated by TOK chemical at 60deg.C for (A)4min, (B)5min, (C)6min, (D)7min.

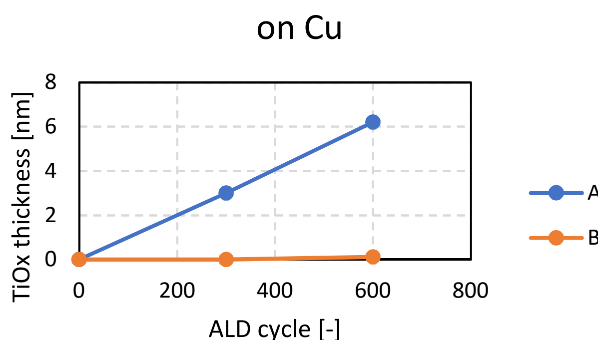

Fig. 4. The relationship between the number of ALD cycles and the TiO_2 thickness on Cu wafer. Coupon A was treated by dHF and citric acid before ALD. Coupon B was treated by dHF, citric acid, and 2 types of TOK chemicals before ALD.

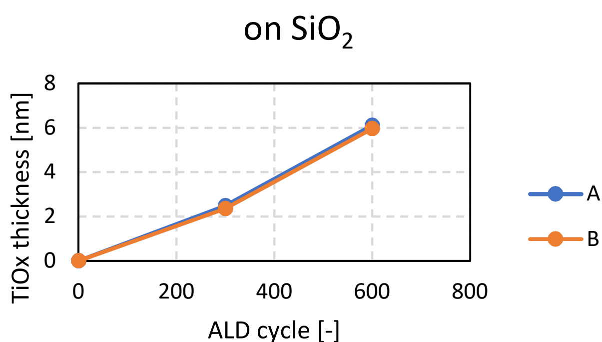

Fig. 5. The relationship between the number of ALD cycles and the TiO_2 thickness on SiO_2 wafer. Coupon A was treated by dHF and citric acid before ALD. Coupon B was treated by dHF, citric acid, and 2 types of TOK chemicals before ALD.

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