

Study of selective atomic layer deposition of Al_2O_3 on Cu/SiO_2 with thiol inhibitors

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The 9th International Conference on Nanomanufacturing (NANOMAN 2024) (Singapore)

KEYWORDS: Atomic layer deposition, Small-molecule inhibitors, Thiols

Abstract Area-selective atomic layer deposition is considered as a key technique in device fabrication down to nanoscale. And thiols are commonly used as inhibitors in area selective deposition (ASD). In this study, the selective adsorption of ET and OT on Cu surfaces was achieved using vapor phase method. Furthermore, the selective atomic layer deposition of Al_2O_3 , utilizing DMAI as the precursor, was successfully demonstrated with SiO_2 as growth area. The findings reveal that inhibitors tend to extend from non-growth area to growth area on patterned samples, thereby destroying the integrity of the Al_2O_3 film. The extent of this migration is influenced by the inhibitor and the pretreatment method employed.

NOMENCLATURE

ET = ethanethiol OT = octanethiol
DMAI = dimethylaluminum i-propoxide

1. Introduction

Atomic layer deposition (ALD) is a vapor-phase film deposition technology known for its excellent large-area uniformity, high conformality, and precisely controllable thickness¹. With the ongoing trend of miniaturization in semiconductor devices, there is an increasing demand for methods that selectively deposit films in specific areas. In semiconductor manufacturing, area-selective deposition (ASD) is emerging as a specialized technology with wide-ranging applications in both the front-end and back-end of line processing². The bottom-up approach of ASD can significantly reduce the number of lithography steps, simplifying the manufacturing process. Additionally, ASD enhances device performance and stability in fully self-aligned via (FSAV) processes by reducing edge placement errors (EPE)³.

ASD methods can be categorized into two types: inherently ASD and template methods⁴. Inherent selective deposition leverages differences in substrate materials to achieve selective adsorption of precursors or co-reactants. Relatively straightforward though, this method imposes strict requirements on the substrate surface and often struggles to maintain selectivity as the number of ALD cycles increases. The template method, which involves forming a passivation layer in

non-growth areas via liquid or gas phase techniques to block subsequent ALD growth, offers greater applicability. Over the past few decades, liquid-phase growth of self-assembled monolayers (SAMs) has been a widely used ASD technique⁵. However, traditional liquid-phase methods can be time-consuming, sometimes requiring several days to achieve the desired effect.

In contrast, gas-phase methods utilizing small molecule inhibitors (SMIs) offer advantages such as rapid reaction times, ease of integration, and compatibility with advanced nanoscale 3D structures⁶. However, due to the short chain lengths of SMIs, the reliability and stability can be insufficient. The blocking mechanism of SMI is not yet fully understood.

Thiols are widely used to achieve selective ALD due to their selective affinity for metals over dielectric materials^{7,8}. The sulfhydryl group in thiols bonds well with metals but exhibits poor bonding with dielectrics, allowing thiols to selectively block ALD processes on metal surfaces⁹. Therefore, understanding the adsorption of thiols on metals and their effectiveness in blocking ALD is of great significance. In this study, ET and OT were selected as inhibitors, and their performance in high-temperature ALD processes was compared and analyzed.

2. ASD using ET and OT as inhibitors

2.1 Materials

ET (>98%, Macklin), OT (>98%, Aladdin), DMAI (>99.9%, Aimou Yuan, Nanjing, China), absolute ethanol (>99.9%, Aladdin), acetic acid (>99.9%, Fisher) are used directly without treatment. Single-sided polished Si wafers (from MAT-CN) with a native oxide layer of approximately 1.8 nm were used as blanket substrates.

2.2 Experimental method

The Cu blanket substrates were prepared by evaporation on silicon wafers. 10 nm chromium was first deposited before 100 nm copper as the adhesive layer in order to increase the adhesion between the evaporated copper and the surface. The evaporation thickness was measured by quartz crystal microbalance provided with the evaporation equipment. Micron patterned substrates were provided by XMC.

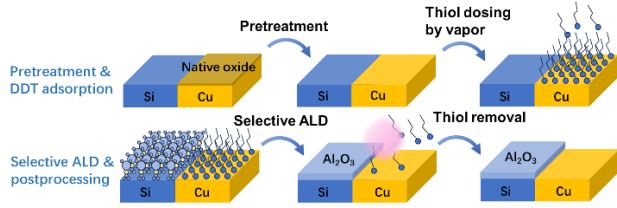


Fig. 1 Schematic diagram of ASD process flow using thiol inhibitors

The ASD process based on thiols is illustrated in Fig. 1. Substrates were first treated with acetic acid for 5 minutes to remove the native oxide layer on the Cu surface, followed by rinsing in ethanol and drying with N₂. The pre-treated substrates were then secured face down onto a bottle cap. Glass bottle containing the inhibitors was heated, allowing the inhibitors to evaporate and adsorb onto the substrates. The heating temperature was controlled using a hot plate. To minimize unwanted physical adsorption in the ALD growth areas, a 10-second N₂ purge was performed after thiol treatment.

The Al₂O₃ atomic layer deposition (ALD) was conducted in a vacuum chamber at 130 °C (MNT, Wuxi, China), with DMAI as precursors, and H₂O as the co-reactant. The DMAI bubbler was heated to 70 °C, while the ultra-pure water was not heated. Ar was used as the carrier gas, with a main flow rate of 300 sccm. Without carrier gas, the base pressure in the ALD chamber was less than 5 Pa. During one ALD cycle, the DMAI pulse time was set to 0.5 seconds, followed by a 15-second argon purge. The ultra-pure water pulse time was 0.2 seconds, followed by a 20-second purge.

Under ALD conditions at 200 °C, substrates were vacuum-sealed in the chamber and heated to minimize oxidation caused by exposure of the Cu sheet to high-temperature air. For post-treatment of the ALD substrates, a hydrogen-argon mixture (10% H₂) was used as the plasma-generating gas to remove thiols. The plasma power was set to 300 W, with a processing time of 10 minutes, and the mixture flow rate was 100 sccm. Annealing at 200 °C was carried out in an HF-Kejing OTF-1200X-S tube furnace. After placing the substrates into the tube furnace at room temperature, the vacuum pump was activated, and the temperature was gradually increased to 200 °C under vacuum. The temperature was held at 200 °C for 30 minutes, then allowed to cool naturally to room temperature in a vacuum environment to prevent oxidation of the substrate at high temperature.

Film thickness was measured using a spectroscopic ellipsometer at a 65° angle (SE, M-200X, J. A. Woollam Co., Inc.), with the alumina Cauchy model used to fit the deposited film thickness. Static water contact angle (WCA) measurements were conducted on blanket substrates, with approximately 2 μL of deionized water brought into contact with the substrate surface to assess changes in surface wettability before and after inhibitor modification and ALD growth. The surface composition and elemental mapping of the patterned substrates were examined using Auger Electron Spectroscopy (AES,

JAMP9510F, JEOL).

2.3 Results and Discussion

First, the effects of heating temperature and duration for ET and OT treatment were studied in Fig. 2. The water contact angle (WCA) of thiol-treated blanket Cu and Si substrates before and after ALD was measured. Following thiol treatment, the WCA of Cu increased to over 100°, while the WCA of the Si surface remained unchanged. This suggests that the thiols selectively adsorb on Cu without affecting SiO₂. Additionally, treatment time and temperature had minimal impact on the WCA, indicating that thiol adsorption has a broad process window.

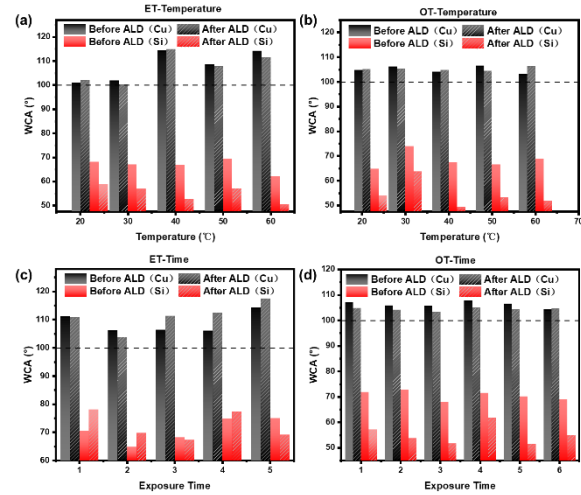


Fig. 2 Water contact angle (WCA) of blanket Cu and Si substrates treated with thiols before and after ALD. (a) Treated with ET at different temperatures for 2min (b) Treated with ET at different temperatures for 2min (c) Treated with ET at 30 °C for different time (d) Treated with OT at 30 °C for different time.

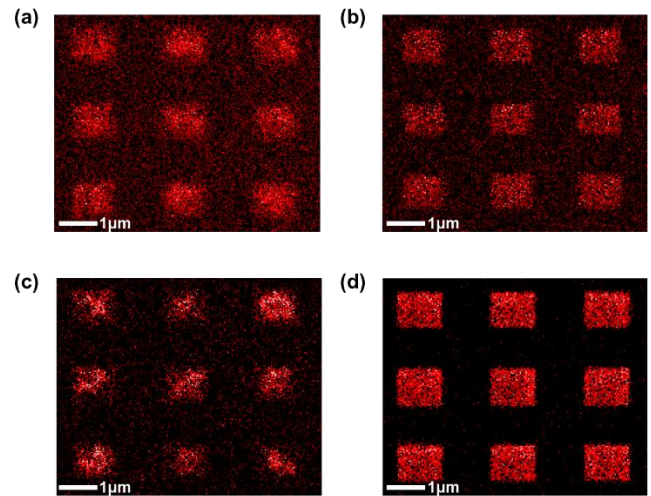


Fig. 3 Al element AES mapping of micron samples treated under different conditions after ALD at 130 °C (a) ET 60 °C-10min (b) ET 30 °C-2min (c) OT 60 °C-10min (d) OT 30 °C-2min

As shown in Fig. 2, full adsorption of ET and OT on the Cu surface can be achieved at a heating temperature close to room temperature (30 °C) with a short treatment time of 2 minutes. Selectivity was further verified on patterned substrates under this condition in Fig. 3. SiO₂ squares with sides of about 1 μm form a 3×3 array on Cu. All patterned samples were treated with thiols and then subjected to 100 cycles of DMAI-H₂O ALD at a cavity temperature of 130 °C. When the inhibitor-treatment temperature is high and the processing time is prolonged, the selectivity of ET and OT on patterned

substrates is suboptimal. Al signals were detected in the non-growth areas of ET-treated substrates, while the OT-treated samples did not completely cover Al_2O_3 in the growth areas. However, at lower heating temperatures and shorter treatment times, Al_2O_3 was correctly deposited in the growth areas, and OT-treated substrates exhibited less Al residue compared to ET-treated ones. Higher temperatures and extended treatment time did not significantly enhance the adsorption of ET and OT on the Cu surface. Instead, these conditions led to poor quality and discontinuity in the Al_2O_3 film within growth areas, likely due to increased physical adsorption. Based on these findings, a heating temperature of 30°C and a treatment time of 2 minutes were chosen as the optimal adsorption conditions for ET and OT.

Next, patterned substrates treated with ET and OT on optimal condition were tested at an ALD deposition temperature of 200°C . Relatively higher temperatures are advantageous for ALD, enabling faster and more stable film growth. Additionally, elevated temperatures help reduce inherent defects and improve the electrical properties of films. Element distribution of patterned substrates was detected by AES in Fig. 4. The red line is scanned from the growth area (SiO_2), while the black line is scanned from the non-growth area (Cu). Although it has been reported that thiols begin to decompose at 200°C ¹⁰, which may result in loss of blocking properties. No Al_2O_3 was deposited on SiO_2 after ET/OT treatment, indicating passivation layer on Cu is working properly. However, no Al signal was detected in the growth area of the patterned substrates treated with ET after ALD. Instead, a weak Cu signal was detected. We hypothesize that the expansion of ET on Cu to adjacent SiO_2 hinders the normal ALD process. At the same time, substrates treated with OT showed obvious Al signal in growth area.

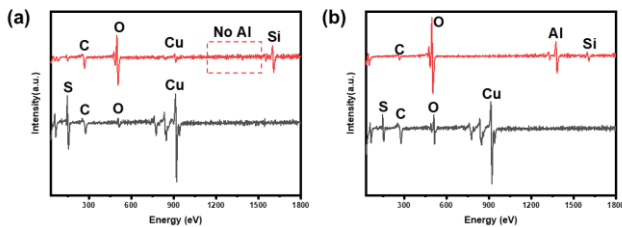


Fig. 4 AES of (a)ET and (b) OT treated patterned substrates after 200°C ALD (one point in each Cu and Si region)

To further investigate the effect on growth area at 200°C , an annealing experiment was further designed to find out the changes in the distribution of OT at high temperature, and the results were shown in Fig. 5. Cu and SiO_2 fringes with a width of about $1\mu\text{m}$ are alternately arranged. The pattern substrate (c) was pretreated with acetic acid, then treated with OT, and finally annealed at 200°C . It shows that after OT treatment, S element is only distributed in the Cu region before annealing at 200°C , which means thiols are not physically adsorbed growth area. However, after annealing, it can be seen from the AES face scan of S element that thiols have expanded from the Cu region to the Si region. In addition, untreated substrates expanded much more severely than samples pretreated with acetic acid. Acetic acid can remove the natural oxide layer on Cu surface¹¹. Oxidation state of Cu surface will affect the growth state of thiols¹². The oxidized Cu tends to form multiple layers of thiols, while the reduced Cu tends to form single layers of thiols¹³. Multilayer thiols may migrate more easily to nearby Si regions at high temperatures.

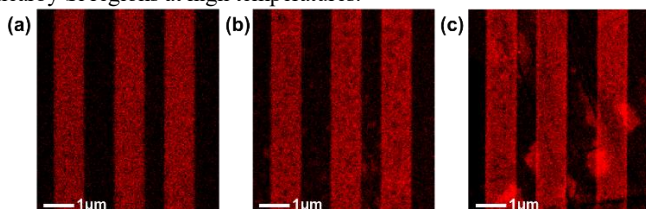


Fig. 5 S signal AES mapping of micron pattern samples treated with

OT. (a) Acetic acid pretreatment (b) Acetic acid pretreatment, annealing at 200°C (c) No Pretreatment, annealing at 200°C

3. Conclusion

ET and OT were used to passivate the Cu surface, successfully achieving area-selective deposition (ASD) at a 130°C ALD temperature, with SiO_2 as the growth area. These results were verified on micron-scale patterned substrates. ET and OT with short chain lengths, are more suitable for lower heating temperature and short processing time. After ALD deposition at a higher temperature (200°C), no Al signal was detected in the SiO_2 region on patterned substrates treated with ET. Only the OT-treated substrate achieved relatively complete Al_2O_3 deposition in the growth area. Subsequent annealing experiments demonstrated that pretreatment methods significantly influence the migration of thiols to adjacent regions at high temperatures, with OT showing less expansion than ET. Additionally, pretreatment with acetic acid cleaning also proved to have a positive effect, resulting in much less OT expansion.

ACKNOWLEDGEMENT

This work is supported by the National Key R&D Program of China (2022YFF1500400), the National Natural Science Foundation of China (51835005, 52273237), the Hubei Province Natural Science Foundation for innovative research groups (2020CFA030) and the Tencent Foundation. The authors would also like to acknowledge the support from the Analytic Testing Center and the Flexible Electronics Research Center of the Huazhong University of Science and Technology.

REFERENCES

1. S. M. George, "Atomic Layer Deposition: An Overview," *Chem. Rev.*, Vol. 110, No. 1, pp. 111–131, 2010.
2. R. Chen, Y.-C. Li, J.-M. Cai, K. Cao, and H.-B.-R. Lee, "Atomic level deposition to extend Moore's law and beyond," *Int. J. Extrem.*, Vol. 2, No. 2, p. 022002, 2020.
3. T.-L. Liu and S. F. Bent, "Area-selective atomic layer deposition of dielectric-on-dielectric for Cu/low-k dielectric patterns," *Advances in Patterning Materials and Processes XXXVI*, 2019.
4. A. J. M. Mackus, M. J. M. Merks, and W. M. M. Kessels, "From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity," *Chem. Mater.*, Vol. 31, No. 1, pp. 2–12, 2019.
5. R. K. Smith, P. A. Lewis, and P. S. Weiss, "Patterning self-assembled monolayers," *Prog. Surf. Sci.*, Vol. 75, No. 1, pp. 1–68, 2004.
6. J. Yarbrough, A. B. Shearer, and S. F. Bent, "Next generation nanopatterning using small molecule inhibitors for area-selective atomic layer deposition," *J. Vac. Sci. Technol. A*, Vol. 39, No. 2, p. 021002, 2021.
7. Hyun Gu Kim, Miso Kim and Bonwook Gu, "Effects of Al Precursors on Deposition Selectivity of Atomic Layer Deposition of Al_2O_3 Using Ethanethiol Inhibitor," *Chem. Mater.*, Vol. 32, No. 20, pp. 8921–8929, 2020.

8. F. S. M. Hashemi and S. F. Bent, "Sequential Regeneration of Self-Assembled Monolayers for Highly Selective Atomic Layer Deposition," *Adv. Mater. Interfaces*, Vol. 3, No. 21, p. 1600464, 2016.
9. A. Kühnle, S. Vollmer, T. R. Linderoth, G. Witte, C. Wöll, And, and F. Besenbacher, "Adsorption of Dodecanethiol on Cu(110): Structural Ordering upon Thiolate Formation," *Langmuir*, Vol. 18, No. 14, pp. 5558–5565, 2002.
10. A. Chandekar, S. K. Sengupta, and J. E. Whitten, "Thermal stability of thiol and silane monolayers: A comparative study," *Appl. Surf. Sci.*, Vol. 256, No. 9, pp. 2742–2749, 2010.
11. K. L. Chavez and D. W. Hess, "A Novel Method of Etching Copper Oxide Using Acetic Acid," *J. Electrochem. Soc.*, Vol. 148, No. 11, p. G640, 20010.
12. "Copper Oxidation Improves Dodecanethiol Blocking Ability in Area-Selective Atomic Layer Deposition." *Adv. Mater. Interfaces*, Vol. 9, No. 19, p. 2200587, 2023.
13. T.-L. Liu, K. L. Nardi, N. Draeger, D. M. Hausmann, and S. F. Bent, "Effect of Multilayer versus Monolayer Dodecanethiol on Selectivity and Pattern Integrity in Area-Selective Atomic Layer Deposition," *ACS Appl. Mater. Interfaces*, Vol. 12, No. 37, pp. 42226–42235, 2020.