Selective atomic layer deposition of zirconium oxide on copper patterned silicon substrate

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Abstract

Selective atomic layer deposition (SALD) was performed on copper patterned silicon substrates using zirconium precursor and ethanol as both an oxygen source and reducing agent. Ethanol targeted copper oxide formed on the copper surface, reverting it back to metallic copper. SALD of metal oxides on silicon surfaces over copper surfaces has been demonstrated up to 2-3 nm, though the process seems to lose its selectivity afterwards. We strive to maintain selectivity to thicker films by stepping away from conventional ALD processes utilizing oxidants. From previous studies with HfO_2 and TiO_2 SALD, we speculate that the oxidation of copper to copper oxide spoils selectivity. In this present study, we carried out oxidant-free ALD by using ethanol as a co-reactant. This process will occur in-situ every 20-30 ALD cycles for ALD of ZrO_2. As expected, reduced ALD growth rate was observed with ethanol compared to that of water or ozone, with a growth rate of about 0.04 nm/cycle on the silicon portion of the substrate.

Introduction

Atomic layer deposition is becoming increasingly popular as a means of depositing films with precise thickness, uniformity, and control on the surface of substrates at the angström level. It has several applications in microelectronics, nanoelectronics, memory storage, and the production of transistors[1], solid oxide fuel cells[2,3], and semiconductors[4]. The ALD process occurs in steps and operates cyclically. Chemicals, called precursors, are injected into the reactor one at a time in a sequential and self-limiting manner. The first precursor is injected, with the help of an inert carrier gas if a metal precursor is used, and reacts with the surface of the substrate. Before the next precursor is injected, inert purging gas is flushed through the reactor to clean the system of any remaining precursor. The next precursor is then injected and reacts with the new surface components on the substrate, with purging gas pulsed right afterwards. This completes the first cycle of several, with film growing gradually with each cycle.

ALD processes help address the challenges faced with conductors, transistors, and memory and fuel cells currently being produced, such as the needs to make gates with high dielectric constant (k) materials and to achieve a particular level of thickness for gate dielectric layers to prevent leakage[5]. Another major challenge that has arisen is the need to find a method to selectively deposit layers onto specific surfaces or portions of surfaces, otherwise known as selective atomic layer deposition (SALD). Efforts made to achieve SALD include the use of molecular masking or self-assembled monolayers (SAMs)[6]. These methods have been successful in preventing deposition in selected areas, but require long assembly and reaction periods. Thus, an emerging, more efficient, and practical method is SALD based on surface physics, surface chemistry, and differences in nucleation times of different materials. This brings in the idea of using patterned surfaces to carry out SALD.

Previous studies have explored the deposition of TiO_2 and HfO_2 films on copper patterned silicon substrates[4,5]. The results from both studies indicate that silicon and copper both had observably different initial nucleation times, with deposits being observed selectively on silicon first. However, as the number of cycles increase, the copper surface undergoes oxidation and deposition is observed. To solve this problem and achieve pure SALD, it has been proposed to pulse a reducing agent through the apparatus following every cycle to reduce copper oxide to metallic copper. Thus, the initial challenge is to select a reducing agent powerful and practical. enough to efficiently ensure SALD.

When considering options for reducing agents, organic options, such as aldehydes, alcohols, ketones, carboxylic acids, hydrogen (gas or plasma), and organometallic agents were considered. From researching several studies[8-15], ethanol was considered a strong reducing agent. Ethanol in vapor gas form was found to be a stronger reducing agent than methanol, another primary alcohol. The additional carbon atom of ethanol produces a greater dipole moment, contributing to greater dipole-dipole interactions between the alcohol and substrate surface. It is also a stronger reducing agent than tertiary alcohols, like tert butanol. The carbon atom to which

the hydroxyl group bonds to in tertiary alcohol does not have valence electrons available to form aldehyde or ketone groups, unlike those of primary or secondary alcohols. Thus, reduction is made difficult, even at temperatures exceeding 385°C[12]. For alcohols, the reduction reaction is easily controlled and also thermodynamically favored at temperatures ranging from 130 - 310°C[13]. Therefore, the use of alcohol as a reducing agent appears more attractive than the conventional thermolysis or hydrogen reduction routes for SALD. Additionally, ethanol has potential to serve dually as an oxygen source. Thus, for the purposes of this study investigating SALD on copper patterned silicon substrates, ethanol can be used to aid in ALD growth through oxidation of the silicon area while combating copper oxide formation as a reducing agent for the copper area.

Experimental

The surfaces of 2 x 2 cm^2 portions of silicon(100) were patterned with 200 nm-thick copper film using electron beam evaporation (Varian model no. NRC3117). Once the wafers were prepared, they were ready to be run through the ALD reactor. The reactor is composed of a quartz tube with a heater. It can operate at temperature up to 600°C. SALD experiments are carried out at 200°C. The ALD reactor operates at a base pressure of less than 20 mTorr. The reactant lines included metal precursor and pure ethanol, with ethanol reacting in vapor form. Argon was used as the carrier gas for the zirconium precursor as well as the purging gas pulsed through the system after injection of zirconium precursor or ethanol vapor. Nitrogen was used as carrier gas for ethanol delivery. The zirconium precursor used was (Tris(dimethylamino)cyclopentadienyl zirconium). Before starting the ALD process, the substrate was treated with ethanol for 5 minutes in-situ. The deposition of zirconium oxide was carried out at a temperature of 200°C and total pressure of 500 mTorr. The thickness of the films developed on the substrates post ALD were measured using a spectral ellipsometer (Woollam M-44). Measuring thickness of the films on the copper patterned portion is difficult to measure with an ellipsometer. Another method proposed was using a four point probe to measure resistivity, with higher resistivity values serving as a strong indicator that deposition has occurred. X-ray photoelectron spectroscopy (XPS, Kratos AXIS-165 equipped with a monochromatic Al Kα (1486.6 eV) X-ray source operating at 15 kV and 10 mA with concentric hemisperical analyzer) was used to analyze zirconium oxide film grown on the surface of the silicon and copper portion of the substrates.

Results and Discussion

Results for zirconium oxide film deposition on silicon using zirconium precursor and ethanol are displayed in Figure 1. Figure 1 is a plot of ZrO_2 film thickness versus the number of ALD cycles. From the figure, it can be seen that film growth increases linearly as the number of ALD cycles increase, which follows patterns of ALD growth kinetics[4]. The growth rate of ZrO_2 films was determined to be 0.04 nm/cycle between 10 and 200 ALD cycles.

In addition to measuring thickness of ZrO_2 films on silicon substrates, X-ray photoelectron spectroscopy (XPS) was carried out for each substrate sample. The XPS data for 50 ALD cycles is displayed in Figure 2 below. It is apparent after 50 cycles that ZrO_2 films have been deposited on the surface of the substrate, with Zr and O peaks being present in the spectra. The peak intensities of Zr and O are also very high in comparison to the less intense Si peak, consistent with ALD of ZrO_2. A carbon peak is also present in the spectra, which could possibly be due to ambient exposure. The intensity of the carbon peak reduced on Ar^+ beam sputtering.

Conclusions

This study attempted to investigate the initial growth rate of ZrO_2 films deposited via SALD on copper patterned silicon substrates. Thin films were deposited onto the surface of these substrates using zirconium precursor, (Tris(dimethylamino)cyclopentadienyl zirconium) and ethanol as a co-reactant. Ethanol served as both an oxidizer to treat the silicon portion of the wafer and a reducing agent, to convert any copper oxide formed back to metallic copper. From the experiments carried out thus far, data have been collected for ALD of ZrO_2 thin films for the silicon portion of these substrates, with a growth rate of 0.04 nm/cycle between 10 and 200 ALD cycles. XPS data for the silicon substrates were also collected, with observably greater peak intensities for Zr and O after 50 ALD cycles. Further studies need to be carried out on the copper portions of these substrates to determine initial nucleation time and the impact of surface chemistry and physics have on film deposition. The results obtained from studies of the copper portion of these substrates will determine whether SALD of ZrO_2 thin films was ultimately successful using ethanol as a co-reactant.

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References

[1] O. Engstrom, B. Raeissi, S. Hall, O. Buiu, M.C. Lemme, H.D.B. Gottlob, P.K. Hurley, K. Cherkaoui, Solid State Electron. 51 (2007) 622.
[2] J.W. Long, B. Dunn, D. R. Rolison, and H.S. White, Chem. Rev. 104. 4463 (2004)
[3] X. Jiang, H. Huang, F.B. Prinz, and S.F. Bent, Chem. Mater, 20, 3897, (2008)
[4] R. Xu, Q. Tao, Y. Yang, C.Takoudis, Thin Solid Films, 520 (2012) 6752–6756
[5] Q. Tao, C. Takoudis, and G. Jursich, Appl. Phys. Lett. 96, 192105 (2010)
[6] X.R. Jiang and S.F. Bent, J. Phys Chem. 113 17613 (2009)
[7] Elam, J. W.; Zinovev, A.; Han, C. Y.; Wang, H. H.; Welp, U.; Hryn, J. N.; Pellin, M. J. Thin Solid Films, 515, 1664 (2006)
[8] G. Dey, S.D. Elliot. J. Phys. Chem. A, 116 (35), pp 8893–8901 (2012)
[9] Z. Li, A. Rathu, R.G. Gordon. Journal of the Electrochemical Society. 153 (11) C787-C794 (2006)

[10] B.S. Lim, A. Rathu, R.G. Gordon, Nature Materials: Harvard University, 2, pp 749-754 (2003)
[11] P. J. Soininen, K.-E. Elers, V. Saanila, S. Kaipio, T. Sajavaara, and S. Haukka, J. Electrochem. Soc. 152, (2), G122-G125(2005)
[12] A.P. Premkumar, N.S. Prakash, F. Gaillard, N. Bahlawane, Materials Chemistry and Physics 125 (3) pp 757-762 (2011)
[13] A. Satta, D. Shamiryan, M.R. Baklanov, C.M. Whelan, Q.T. Le, G.P. Beyer, A. Vantomme, K. Maex, J. Electrochem. Soc. 150, 5, G300-G306 (2003)
[14] J. A.T. Norman, M. Perez, S. E. Schulz, T. Waechtler, Microelectron. Eng. 85, 2159-2163 (2008)
[15] K. L. Chavez, D. W. Hess, J. Electrochem. Soc. 148. 11. G640-G643 (2001)

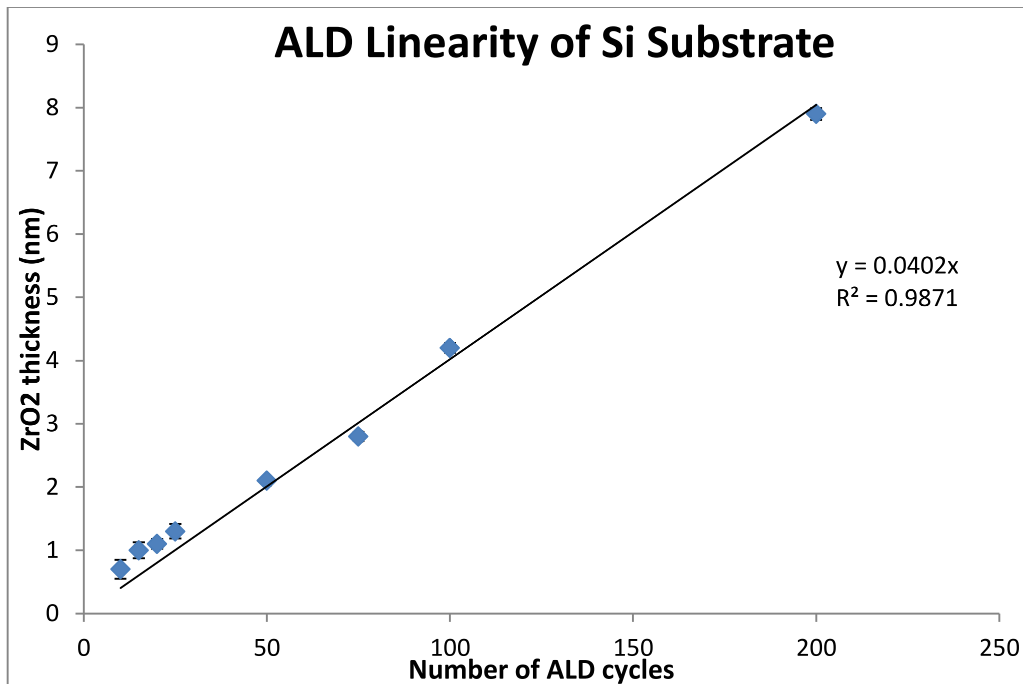

Figure 1: ZrO_2 thickness versus number of ALD cycles on silicon substrate. The linearity observed in this figure indicates that ALD occurred as predicted. ALD reactor temperature was 200 °C and base pressure was 500 mTorr.

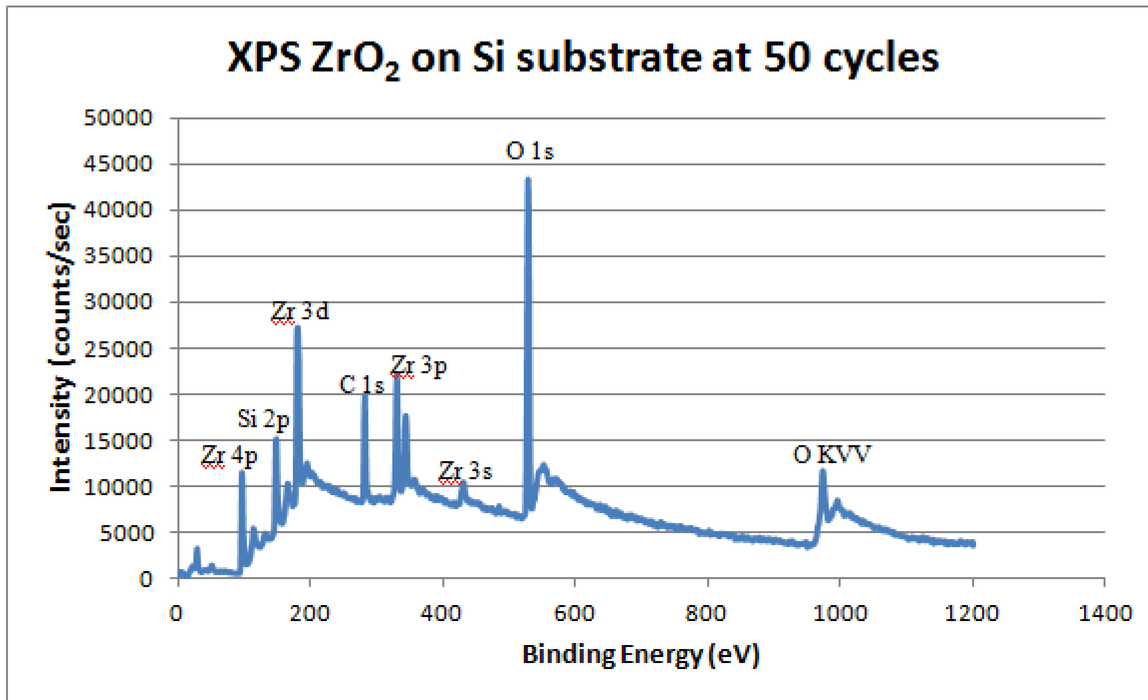

Figure 2: XPS of ZrO_2 deposited film on silicon substrate at 50 ALD cycles. Zirconium and Oxygen peaks are clearly present in the spectra, indicating the zirconium oxide films have been deposited on the surface of the silicon substrates after 50 ALD cycles.