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Room-temperature atomic layer deposition of ZrO₂ using tetrakis(ethylmethyldamino)zirconium and plasma-excited humidified argon

K. Kanomata ^{a,b}, K. Tokoro ^a, T. Imai ^a, P. Pansila ^a, M. Miura ^a, B. Ahmmad ^a, S. Kubota ^a,

K. Hirahara ^a, F. Hirose ^{a,*}

^a Graduate School of Science and Engineering, Yamagata University,

4-3-16 Jonan, Yonezawa 992-8510, Japan

^b Japan Society for the Promotion of Science

5-3-1 Kojimachi, Chiyoda-ku, Tokyo 102-0083, Japan

* Electronic mail: fhirose@yz.yamagata-u.ac.jp

Abstract

Room-temperature atomic layer deposition (ALD) of ZrO_2 is developed with tetrakis(ethylmethylamino)zirconium (TEMAZ) and a plasma-excited humidified argon. A growth per cycle of 0.17 nm/cycle at room temperature is confirmed, and the TEMAZ adsorption and its oxidization on ZrO_2 are characterized by IR absorption spectroscopy with a multiple internal reflection mode. TEMAZ is saturated on a ZrO_2 surface with exposures exceeding $\sim 2.0 \times 10^5$ Langmuir (1 Langmuir = 1.0×10^{-6} Torr·s) at room temperature, and the plasma-excited humidified argon is effective in oxidizing the TEMAZ-adsorbed ZrO_2 surface. The IR absorption spectroscopy suggests that Zr-OH works as an adsorption site for TEMAZ. The reaction mechanism of room-temperature ZrO_2 ALD is discussed in this paper.

1. Introduction

Zirconium oxide (ZrO_2) is a well-known material for coating. Since ZrO_2 allows an excellent transparency to the light, ranging from near-infrared to visible, due to its wide band gap of ~ 5.4 eV [1], it is applicable as coating films for high refractive index mirrors and broadband interference filters [2]. ZrO_2 has also been examined for coating on carbon nanotubes for chemiluminescent sensors [3]. On the other hand, ZrO_2 has been also examined as anticorrosion coating for steels [4]. In the field of very large-scale integration production, the scaling down of SiO_2 -gate metal-oxide semiconductor field effect transistors is reaching its limit in terms of the gate leakage current. Hence, various high- k gate dielectric materials are being examined. ZrO_2 is believed to be a candidate because of the high relative dielectric constant of ~ 43 in the crystallized ZrO_2 and a high thermal stability at the interface with Si [5]. To extend the applicability of ZrO_2 , its deposition at low temperatures is required since the ZrO_2 coating might provide an excellent chemical stability for soft, non-heat tolerant materials.

Atomic layer deposition (ALD) is a technology for depositing oxide films with a monolayer precision. It consists of repeated cycles of saturated adsorption of a source gas on a substrate, followed by the surface reactivation before the next adsorption cycle [6]. The growth temperature for ZrO_2 deposition is desired to be decreased to near room temperature (RT) because the interfacial layer on the substrate might be formed by a solid phase reaction

during the heating process [7]. There is also a demand for flexible electronic devices that are fabricated on soft materials such as polyimide and polyethylene terephthalate films, notwithstanding high temperatures.

ALD was developed to uniformly deposit thin-film oxides onto substrates of varying compositions at low temperatures. In case of ZrO_2 , using zirconium t-butoxide $[\text{Zr}(\text{OC}_4\text{H}_9)_4]$ and oxygen, a deposition temperature of around 300 °C was reported [8]. Zirconium tetrachloride (ZrCl_4) and water vapor based ALD was also examined with a deposition temperature of 300 °C [7]. J. Aarik *et al.* reported the chloride based ALD of ZrO_2 in a wide temperature range from 180 to 600 °C [9]. On the other hand, by using tetrakis (ethylmethylamino) zirconium (TEMAZ) and ozone, the deposition temperature was reported to be around 250 °C [10]. Hausmann *et al.* [11] reported a low temperature ALD down to 50 °C with TEMAZ and water vapor, although the RT process has not been released. To decrease the growth temperature, plasma-excited oxidizing agents have been utilized [12-14]. For ZrO_2 , Yun *et al.* [15] reported plasma-enhanced ALD using TEMAZ and with O_2 plasma where it was performed at 110 °C. On the other hand, Lee *et al.* [16] reported ultra violet (UV) light-enhanced ALD using zirconium t-butoxide $[\text{Zr}(\text{OC}_4\text{H}_9)_4]$ and water vapor where the RT deposition was achieved. However, this RT ALD is difficult to be applied to conformal coating because the UV enhanced method does not allow for the conformal light irradiation on the complicated surfaces.

To decrease the deposition temperature, the plasma-excited water vapor and Ar (humidified Ar) is used in this work. Previously we reported RT-ALD of SiO₂ with tris(dimethylamino)silane (TDMAS) and the same oxidizing agent with remote plasma system. It was demonstrated that the plasma method was effective in oxidizing the precursor-adsorbed surface while producing OH sites for TDMAS adsorption [14]. We previously discussed the role of hydroxylation in enhancing the adsorption probability of TDMAS on the SiO₂ surface at RT [17, 18]. With the plasma excited humidified argon, we also developed the RT ALD of TiO₂ with a precursor of tetrakis(dimethylamino)titanium [19]. On the other hand, we also tried to achieve the RT ALD of HfO₂ with tetrakis(ethylmethylamino)hafnium (TEMAH) although we found that plasma excited humidified argon was ineffective [20]. Here we newly introduced the plasma excited humidified oxygen. In this study, we achieved a growth per cycle (GPC) of 0.26 nm/cycle at RT and found that the surface hydroxyl groups play a role of the adsorption site for TEMAH.

In this paper, we developed the RT ZrO₂ ALD using TEMAZ with the plasma-excited humidified argon. We show a ZrO₂ GPC of 0.17 nm/cycle with this method. The fundamental reactions in precursor adsorption and oxidization on ZrO₂ are investigated by multiple-internal-reflection infrared absorption spectroscopy (MIR-IRAS). We find that the OH site is consumed as the adsorption site in the TEMAZ adsorption and the plasma excited humidified argon effectively introduces the OH sites on the ZrO₂ surface. In this paper, we discuss the

mechanism of the RT-ALD of ZrO_2 with the plasma-excited humidified argon. We also discuss the difference in the ALD mechanism between ZrO_2 and HfO_2 with the plasma enhanced methods.

2. Experimental methods

Fig. 1 shows a schematic diagram of the ALD chamber. It consists of a stainless steel chamber, with a turbo molecular pump, and a gas delivery system. TEMAZ is introduced into the ALD chamber using a variable leak valve, and the TEMAZ exposure ranged to 2.0×10^5 Langmuir ($1 \text{ L} = 1.33 \times 10^{-4} \text{ Pa}\cdot\text{s} = 1.0 \times 10^{-6} \text{ Torr}\cdot\text{s}$) during the adsorption step in the ALD cycle. The pressure of TEMAZ in the chamber was measured by an uncalibrated B-A gauge. A plasma-excited humidified argon source was also connected to the chamber. The source gas for the plasma-excited humidified argon, generated by a water bubbler, was a mixture of water vapor and Ar. The bubbler temperature was 60°C . The Ar gas flow rate was set at 10 sccm, and the net flow rate of the water vapor is estimated to be 1.96 sccm. The plasma was generated in a glass tube using an induction coil with a frequency of 13.56 MHz and a radio-frequency (RF) power of 30 W. In this system, the Ar introduction in the tube is effective in stabilizing the plasma in it. We also assume that the Ar gas works as the carrier gas for plasma excited species from the water vapor.

The present ALD process consists of the TEMAZ irradiation on the growing surface, followed by the oxidization. The TEMAZ irradiation time was 225 s, where the TEMAS

exposure to the sample surface is estimated to be 203007 L. During the TEMAZ irradiation, the partial pressure of TEMAZ in the ALD chamber was kept to be 0.19 Pa to avoid the precursor condensation. The plasma-excited humidified argon was introduced for 300 s during the oxidation step. The chamber is evacuated for 90 or 60 s to exchange the process gas between the TEMAZ and plasma-excited humidified argon injections. During this process, the substrate temperature is kept at 25 °C.

We used a p-type Si(100) substrate as the sample with resistivities from 8 to 10 $\Omega\cdot\text{cm}$. Before installed to the chamber, the sample was cleaned with a buffered HF acid solution, which produces an H-terminated surface [21]. The sample was treated with the plasma-excited humidified argon in the ALD chamber at a plasma power of 20 W for 5 min for cleaning. After the ALD process, the ZrO_2 growth thickness was measured by spectroscopic ellipsometry (JASCO M-220). The oxidization status of Zr in the grown film was characterized by X-ray photoelectron spectroscopy with an Mg-K α X-ray source. The take-off angle of the photoelectron was 90° with respect to the sample surface.

The TEMAZ adsorption on the ZrO_2 surface and the oxidization at RT (25 °C) were observed by multiple-internal-reflection infrared absorption spectroscopy (MIR-IRAS). This technique is sensitive to the surface adsorbates and has a high energy resolution of 4 cm^{-1} . We used the prism samples with a size of $0.5 \times 10 \times 40 \text{ mm}^3$ and 45° bevels on each of the short edges. IR radiation from an interferometer (ABB-BOMEM FTLA-2000) was

introduced onto one of the two bevels of the sample; the radiation was reflected internally about 80 times [22, 23]. The IR radiation that exited the other bevel was focused onto a liquid-nitrogen-cooled InSb detector. We recorded here changes in the surface atomic structure identified by IRAS during the ALD processes of precursor adsorption and humidified argon plasma treatment. To calculate a particular IR absorbance spectrum, we first measured an IR transmission spectrum before the process as a base spectrum and then recorded a second IR transmission spectrum after the specific process. The IR transmittances before and after the process, I_r and I_o , respectively, were used to calculate the absorbance (A_{bs}) from $A_{bs} = \log_{10}(I_r/I_o)$. The absorbance spectrum indicates only the change induced by the specific process. Similar analyses can be found in other papers on MIR-IRAS [22, 23].

3. Results and discussion

3-1. Reaction mechanism

To observe the adsorption of TEMAZ on ZrO_2 , IR absorbance spectra were measured from the TEMAZ-adsorbed ZrO_2 surface, as shown in Fig. 2. The initial ZrO_2 surface was made by depositing ZrO_2 on a Si (100) prism surface by the present ALD method to a thickness of 2.5 nm. The TEMAZ exposure ranged from 1.0×10^4 to 6.0×10^5 L. We can see the clear increase of hydrocarbon introduced by the TEMAZ molecule at wavenumbers of 2966, 2931, 2869, and 2781 cm^{-1} . The peaks at 2966 and 2869 cm^{-1} can be assigned to the

-CH_3 groups [20, 24]. The peak at 2931 cm^{-1} can be assigned to the -CH_2 groups [20, 24]. The peak at 2781 cm^{-1} comes from the symmetrical stretching vibration of $\text{-N(C}_2\text{H}_5\text{)(CH}_3\text{)}$ [20, 24]. To confirm the saturated adsorption, absorbance of C-H at 2869 cm^{-1} as a function of the TEMAZ exposure is shown in Fig. 3. In this experiment, we used two kinds of starting surfaces: SiO_2 and ZrO_2 . The initial SiO_2 surface was prepared from thermally cleaned Si(100) with the present plasma-excited humidified argon treatment. The treatment time was 5 min. The TEMAZ adsorption on SiO_2 was investigated to evaluate the initial adsorption of TEMAZ on Si as the starting surface for ZrO_2 ALD on Si. We can see that the saturation of TEMAZ takes place at exposures exceeding $3.0 \times 10^5\text{ L}$ on both SiO_2 and ZrO_2 surfaces. The ZrO_2 surface requires a smaller saturation exposure compared with that for SiO_2 . This indicates that the adsorption coefficient of TEMAZ on ZrO_2 is higher than that on SiO_2 . This experiment suggests that TEMAZ exposure can be set to be higher than $3.0 \times 10^5\text{ L}$ only for the initial growth on Si while it is possible to decrease the exposure to $2.0 \times 10^5\text{ L}$ on the ZrO_2 surface in the ZrO_2 ALD on Si.

To assume an adsorption model of TEMAZ on the ZrO_2 surface, we plotted the variation in -CH_3 group absorbance of 2869 cm^{-1} as a function of the TEMAZ exposure, and fitted it with a simulation. The simulation was used to obtain the number of sites required for the precursor adsorption. If we assume that TEMAZ adsorbs to the surface by consuming a

single adsorption site, the normalized coverage θ and the exposure L are written by the Langmuir isotherm equation

$$\theta = 1 - \exp(-k_1 L) \quad (1)$$

where k_1 is a reaction constant. If we assume the two-site adsorption, the equation is written as

$$\theta = 1 - \frac{1}{1+k_2 L} \quad (2)$$

k_2 is also the reaction constant [25]. Using Eqs. (1) and (2), we fitted the calculation to experimentally obtained $-\text{CH}_3$ group absorbances by changing k_1 and k_2 , as shown in Fig. 4. Here k_1 and k_2 were 2.4×10^{-5} and 3.9×10^{-5} , respectively. It was found that the two-site adsorption model gives a better fit. This experiment clearly indicates that TEMAZ requires two adsorption sites to adsorb on the ZrO_2 surface.

To evaluate the oxidization mechanism, the plasma excited humidified argon was irradiated on the TEMAZ saturated ZrO_2 surface at room temperature. In this experiment, the TEMAZ exposure was set at 6.0×10^5 L. The IRAS spectra are shown in Fig. 5. As the treatment time of the plasma gas is increased, the negative peak becomes prominent. In Fig. 6, the decrease in the C-H absorbance at 2869 cm^{-1} as a function of the plasma treatment time is plotted. The C-H absorbance decreases sharply for the first 1 min and its change becomes smaller at exposures in excess of 2 min. We can say that the initially adsorbed hydrocarbon

with the 6.0×10^5 L exposure of TEMAZ was completely removed with the 5 min plasma treatment.

To discuss the reaction mechanism, the identification of adsorption site is important. As we can see in the previous studies for the adsorption sites [19, 20], the hydroxyl groups are expected as the adsorption sites. We monitored the absorbance of the surface hydroxyl group by MIR-IRAS for the TEMAZ and plasma treatments as shown in Fig. 7. With the TEMAZ saturation at RT on ZrO_2 , the decrease of the hydroxyl group at 3672 cm^{-1} [26] is confirmed while it is recovered with the plasma treatment. This indicates that the OH group is the adsorption site for TEMAZ and it is recovered with the present plasma treatment.

Based on the surface investigation, we assumed possible adsorption and oxidization models for the present ZrO_2 ALD as shown in Fig. 8. The adsorption of TEMAZ can be written as,

In Eq. (3), we assumed that the dissociated $\text{Zr}[\text{N}(\text{C}_2\text{H}_5)(\text{CH}_3)]_2$ molecule adsorbs on the ZrO_2 surface with two OH sites. After the adsorption step, the surface is covered with the hydroaminocarbon of $\text{Zr}[\text{N}(\text{C}_2\text{H}_5)(\text{CH}_3)]_2$. Here the evolution of hydrocarbon and $\text{N}[(\text{C}_2\text{H}_5)(\text{CH}_3)]_2$ and the degeneration of the $-\text{OH}$ peaks in IR absorbance spectra can be explained consistently. In the oxidization process, we assumed that the oxidizing agents of O

and OH are produced from plasma-excited humidified argon. When the plasma-excited humidified argon is injected to the saturated surface, all the hydroaminocarbons are assumed to be replaced with OH radicals as follows:

It is also assumed that all the hydroaminocarbons released from the surface are oxidized to CO_2 , N_2O , and H_2O .

3-2. ALD experiment

Fig. 9 shows the ZrO_2 thickness as a function of ALD growth cycles. A linear relationship between the thickness and cycle number is confirmed. The GPC is estimated to be 0.17 nm/cycle that is comparable with that in the conventional thermal ZrO_2 ALD (0.11 nm/cycle) [27].

From the ALD-grown ZrO_2 , we evaluated the oxidation status of Zr and residual N by x-ray photoelectron spectroscopy, as shown in Fig. 10. In this experiment, the ZrO_2 surface was etched to the depth of ~1 nm by means of Ar sputtering. We confirmed significant photoelectron peaks of Zr and O. The N 1s peak at ~398 eV indicates that N in the TEMAZ was not removed thoroughly by the plasma-excited humidified argon. The C and N concentrations in the ZrO_2 were estimated to be 10 and ~3 %, respectively.

To observe the oxidization state of Zr in RT-ALD grown ZrO_2 , we measured the Zr 3d photoelectron spectra for samples made at 30 and 120 cycles, as shown in Fig. 11. The presence of Zr 3d $_{5/2}$ peak is confirmed at around 181.7 eV, which indicates that the zirconium atoms in ZrO_2 were fully oxidized [28].

In this work, we achieved room temperature ALD of ZrO_2 with the plasma-excited humidified argon, although the deposited film is contaminated with C and N. To suppress the contamination level, the post annealing in the oxidizing environment might be effective. There is also a room for optimizing the plasma power in the oxidizing step, since the higher density of OH and O radicals must be effective in removing the residual carbon. We are now continuing the process tuning and the related results will be published elsewhere.

3-3. Discussion

In the present study, we confirmed that the TEMAZ saturation exposure of 2.0×10^5 L on the ZrO_2 surface is much higher than that of TDMAS on SiO_2 [17]. The low saturation exposure of 4000 L for TDMAS on SiO_2 was reported, where it was concluded that TDMAS preferentially adsorbs at the OH site [17]. As a possible explanation of the high saturation exposure for TEMAZ, we can consider the molecular stability. TEMAZ is a symmetrical molecule where the zirconium atom is bonded to four aminocarbons, with the formula of $\text{N}[(\text{C}_2\text{H}_5)(\text{CH}_3)]$. TDMAS is an asymmetrical molecule with three aminocarbons and

hydrogen. It is possible that the high molecular stability of TEMAZ resulted in the lower reaction rate for the adsorption, which might affect the saturation process of the precursor.

We made almost the same discussion in the HfO₂ ALD using TEMAH [20].

In our previous study, the room-temperature HfO₂ ALD was developed by using TEMAH and the plasma excited humidified oxygen (water vapor and oxygen) [20]. In this study, it was reported that TEMAH, having a similar chemical structure to TEMAZ, has a saturation behavior on hydroxylated HfO₂ surfaces with its exposure of 1.0×10^5 L. We can say that TEMAZ and TEMAH have almost the same adsorption characteristics in RT ALD. What is different about them for the RT ALD is the reactivation method. The HfO₂ RT-ALD requires the stronger oxidization gas of the plasma excited humidified oxygen. We assume that this difference is caused from difference in the strength of the metal-N bonding in the precursors although the quantum chemistry simulation must be necessary for further discussion.

In the present ALD experiment, we obtained a higher growth rate (0.17 nm/cycles) compared with that in the conventional plasma ALD, for which a ZrO₂ growth per cycle of 0.14 nm/cycle was reported by Yun *et al* [15]. We assumed that present ZrO₂ is not so dense compared with the ZrO₂ film made with the conventional ALD process, because the present film is amorphous due to its low growth temperature. The refractive index of our ZrO₂ film was measured to be 1.77 at 580 nm, which is slightly lower than 1.87 for amorphous ZrO₂,

reported elsewhere [29]. The density of the present ZrO_2 film is estimated to be 3.6 g/cm^3 [30]. To improve the density, we assume that the rapid thermal annealing might be effective.

4. Conclusions

To conclude, we developed a RT ZrO_2 ALD method with a precursor of TEMAZ and a plasma-excited humidified argon as the oxidizing agent. The adsorption of TEMAZ on the ZrO_2 surface and its oxidization by the plasma-excited humidified argon were studied by MIR-IRAS. The plasma-excited humidified argon was effective in oxidizing the TEMAZ-adsorbed ZrO_2 surface while producing adsorption sites of Zr-OH for further TEMAZ adsorption on the growth surface. The IRAS measurement evidenced clear saturation of the TEMAZ adsorption and its oxidization at RT. A growth per cycle of 0.17 nm/cycle was confirmed at RT. The results of the present study provide a deep insight into the fabrication of thin ZrO_2 films for flexible and organic electronics.

Acknowledgement

This work was partly supported by JSPS KAKENHI Grant Numbers 15H03536, 15K13299 and 26·10615. It was also partly supported by JST-CREST. We would like to express the deepest appreciation to AIR LIQUIDE for offering the high quality precursor of TEMAZ.

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Figure Captions

Figure 1. Schematic diagram of RT ALD system for ZrO_2 deposition.

Figure 2. IR absorbance spectra obtained from TEMAZ-adsorbed ZrO_2 films for various amounts of TEMAZ exposure (in L) where the surface was treated with plasma - excited humidified argon before the adsorption. The initial ZrO_2 thickness was 2.5 nm.

Figure 3. Variation in the C-H absorbance at 2869 cm^{-1} as a function of TEMAZ exposure obtained from the TEMAZ-adsorbed ZrO_2 and SiO_2 surfaces. The initial ZrO_2 surface was prepared by the RT-ALD with a thickness of 2.5 nm. The initial SiO_2 surface was prepared by Si(100) treated with the present plasma-excited humidified argon.

Figure 4. Normalized C-H absorbance peak at 2869 cm^{-1} as a function of TEMAZ exposure, calculated from IR absorbance spectra measured for the TEMAZ-adsorbed surface. The experimental data were fitted with simulations with the one- and two-site adsorption models.

Figure 5. IR absorbance spectra obtained from the TEMAZ-adsorbed ZrO_2 films after the surface was treated with plasma-excited humidified argon for periods ranging from 1 to 20 min.

Figure 6. Variation in the C-H absorbance at 2869cm^{-1} for the TEMAZ saturated ZrO_2 surfaces during plasma-excited humidified argon treatment.

Figure 7. IR absorbance spectra obtained from the TEMAZ adsorbed and plasma-excited humidified argon treated ZrO_2 surfaces.

Figure 8. Reaction model of TEMAZ adsorption and oxidization for the RT ALD of ZrO_2 . R_1 and R_2 denote CH_3 and C_2H_5 , respectively.

Figure 9. ZrO_2 growth thickness as a function of the ALD cycle number.

Figure 10. X-ray photoelectron wide-scan spectrum of the ZrO_2 film on Si, produced by 120 cycles of room temperature ALD, after which the sample surface was etched by Ar bombardment to a depth of 1 nm to remove the naturally adsorbed carbon and water.

Figure 11. X-ray photoelectron spectrum of Zr_{3d} measured from the ZrO_2 film produced by the RT ALD, for samples made at 30 cycles (dashed line) and 120 cycles (solid line).

Figure1

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Figure2

Fig. 2

Figure3

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