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HIGHLIGHT

Atomic layer deposited HfO_2 and HfO_2/TiO_2 bi-layer films using a heteroleptic Hf-precursor for logic and memory applications

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HfO_2 films were grown by atomic layer deposition (ALD) using a new heteroleptic hafnium precursor, *tert*-butoxytris(ethylmethylamido)hafnium (BTEMAH), and ozone. This BTEMAH precursor achieved a very high growth rate and retained excellent thermal stability in electrical performance due to the high film density of the HfO_2 films. Additionally, the structural compatibility between the specific planes of tetragonal HfO_2 and rutile TiO_2 achieved a high dielectric constant (~29) for HfO_2 films grown on a rutile TiO_2 film. It is demonstrated that this BTEMAH is a very promising precursor for the growth of HfO_2 films for both the applications of a gate oxide and a capacitor dielectric.

HfO_2 has been extensively studied as an alternative gate dielectric for the replacement of SiO_2 owing to its outstanding properties such as a reasonably high dielectric constant, wide band gap (5.68 eV), and excellent thermal stability on a silicon surface.[1] These properties of HfO_2 that make it a leading material for a gate oxide in complementary metal-oxide-semiconductor devices also give it strong potential for its use as a capacitor dielectric of dynamic random access memory (DRAM) devices.

Atomic layer deposition (ALD) is considered as the most promising method for the growth of HfO_2 films on account of its excellent thickness control and good interface engineering properties. There are many precursors that have been examined for the growth of HfO_2 films.[2–10] Although $HfCl_4$, one of the most common Hf precursors, shows a wide ALD window, the growth rate of HfO_2 films grown by $HfCl_4$ is only ~0.05 nm per cycle.[2–4] Such a slow growth rate induces relatively severe interfacial reaction with the substrate during the ALD owing to the prolonged process time.[2] Recently, alkylamide precursors have attracted much attention as an alternative Hf precursor for the growth of HfO_2 films.[5–9] These precursors form a $Si(O)N_x$ layer at the interface between HfO_2 and Si during film growth because of the N atoms

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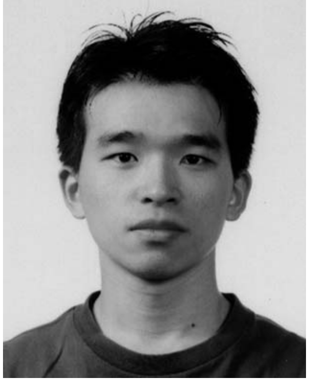

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contained in these precursors, which leads to good interfacial properties.[9] Although these precursors show a growth rate of approximately 0.1 nm per cycle,[5–9] the value is still inadequately low. Another ALD process reported, using a modified cyclopentadienyl (Cp) Hf precursor [$(CpMe)_2HfMe_2$ and $(CpMe)_2Hf(OMe)Me$], shows a wide ALD window up to 500 °C. For other modified cyclopentadienyl Hf precursor [$Cp_2Hf(OMe)_2$ and $(CpMe)_2Hf(OMe)_2$], the ALD temperature was limited to 350 °C. However, the growth rate is as low as 0.05 nm per cycle.[10]

In this highlight article, the authors' recent results on the high growth rate and highly promising properties of the ALD HfO_2 films using a new type of precursor, *tert*-butoxytris(ethylmethylamido) hafnium [$HfO^tBu(NEtMe)_3$, BTEMAH], are summarized.[11] The growth rate of the HfO_2 films grown from BTEMAH is approximately 0.16 nm per cycle at 300 °C, which is the highest value reported for the ALD of HfO_2 so far.[11] In addition, the films grown from BTEMAH show excellent thermal stability in electrical performance due to their high film density. The results for the HfO_2 film grown from BTEMAH as a capacitor dielectric are summarized as well in this article. Although the HfO_2 films are crystallized on Si substrates into a monoclinic phase, the authors found that the HfO_2 films grown on a rutile TiO_2 surface are known to have a mixture of tetragonal and amorphous phases.[12] The mixed matrix has a high dielectric constant due to the contributions from the higher-k tetragonal phase. This HfO_2/rutile TiO_2 stack shows excellent electrical properties.

The growth rates of HfO_2 films grown by ALD with common Hf precursors are normally reported to be around 0.1 nm per cycle at maximum.[5–9] However, the HfO_2 films grown by the BTEMAH precursor and ozone showed a high growth rate of 0.16 nm per cycle at a growth temperature of 300 °C, which is the highest value reported so far (Fig. 1(a), squares). The high growth rate of this precursor compared to others is a crucial merit for mass-production. Fig. 1(a) also shows the change in the physical thickness (circles) of the films grown from tetrakis (dimethylamido)hafnium (TDMAH) and ozone, one of the most common precursors, as a function of the number of cycles at the same temperature for the purpose of clearly showing the high growth rate of the HfO_2 grown from BTEMAH. The growth rate calculated from the slope is 0.1 nm per cycle, which is much lower than the value of the HfO_2 grown from BTEMAH and ozone.

The growth rate of ALD generally depends on areal density of chemisorption sites on the surface and molecular bulkiness of the precursors. Since TDMAH and BTEMAH give the same films of HfO_2, the density of chemisorption sites on the growing surface may not be so significantly different that it may result in such a large difference in their growth rates. Furthermore, the BTEMAH precursor is rather bulkier than TDMAH due to the presence of the *tert*-butoxy ligand. It is believed that the unusual high growth rate of HfO_2 film from BTEMAH may be contributed by partial thermal decomposition of the chemisorbed BTEMAH molecules. It is well-known that the *tert*-butoxy ligand is vulnerable to thermal decomposition, which is the reason for $Hf(O^tBu)_4$ not being suitable as an ALD precursor.[13] Although BTEMAH contains the *tert*-butoxy ligand, the thickness increase owing to the thermal decomposition is smaller than 0.5 nm when BTEMAH is continuously exposed to a substrate for 500 s at 300 °C (data not shown). However, when the exposure of BTEMAH is coupled with its purging step (cyclic exposure), the film thickness increased significantly. For example, when the BTEMAH exposure (2 s) and its purging (60 s) steps were repeated at 300 °C for 100 cycles (totally 200 s of BTEMAH exposure) without any oxygen source supply/purge steps, HfO_2 film with a thickness of ~7 nm was deposited. Even more interestingly, the film thickness was not increased by increasing the BTEMAH exposure time in the cyclic exposure method, suggesting that the thermal decomposition of BTEMAH is self-limiting.

Generally if a precursor is thermally decomposed during the ALD process, it cannot be used as a plausible precursor for ALD due to non-uniform chemical vapor deposition (CVD)-like behavior. Even though BTEMAH thermally decomposed at least partially, it can give a high growth rate by the ALD process

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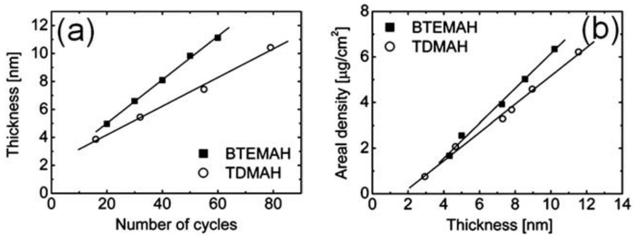

Fig. 1 (a) Change in the thickness of HfO$_2$ films grown from BTEMAH and TDMAH as a function of number of cycles, respectively, (b) change in the areal density of Hf ions in the films grown from BTEMAH and TDMAH as a function of the film thickness, respectively. Reproduced from Ref. 11, http://dx.doi.org/10.1039/B806382F. Reproduced by permission of the Royal Society of Chemistry.

possibly owing to the self-limiting nature of the partial thermal decomposition. The accurate mechanism for such a self-limiting thermal decomposition and a purge-step dependent growth is not understood as yet. However, the partial removal of the bulky ligands may enhance the chemical adsorption of the precursor, and a higher growth rate was achieved.

HfO$_2$ films grown from BTEMAH showed a high film density despite the high growth rate. Fig. 1(b) shows the change in the areal density of Hf ions in the films grown from BTEMAH (squares) and TDMAH (circles) as a function of film thickness. Although the areal density of Hf ions in both cases linearly increased with film thickness, the slope depends on the type of the precursor. The Hf density of the films calculated from the slope is 7.6 and 6.2 g cm^{-3} for BTEMAH and TDMAH, respectively. (The ideal Hf density of bulk HfO$_2$ is 8.21 g cm^{-3}.) This suggests that the high growth rate of the BTEMAH HfO$_2$ films does not result from the formation of porous films, and also that BTEMAH is able to grow denser HfO$_2$ films compared to conventional precursors.

The formation of denser HfO$_2$ films from BTEMAH makes this precursor favorable for the growth of HfO$_2$ films, especially in gate oxide applications. The growth of HfO$_2$ films on Si substrates normally results in the formation of an interfacial layer with a low dielectric constant. Although both the films grown from BTEMAH and TDMAH have an interfacial layer, the interfacial layer of the HfO$_2$ films grown from BTEMAH is relatively thinner compared to the interfacial layer of the films grown from TDMAH. Additionally, the interfacial layer of the films grown from TDMAH has a larger Hf content than the interfacial layer of the films grown from BTEMAH.[11] This suggests that the diffusion of Hf atoms into the layer is more serious in the case of TDMAH HfO$_2$, which is due to its relatively lower film density.

The high density of the HfO$_2$ films grown from BTEMAH also retards the crystallization of the films during post-annealing.[11] Fig. 2 shows high resolution transmission electron microscopy (HRTEM) images of as-grown HfO$_2$ films from BTEMAH and the films annealed at 700 and 1000 °C for 1 min. To compare the crystallization property of the films, HRTEM images of the HfO$_2$ films grown from TDMAH annealed at corresponding temperatures are also shown in Fig. 2. Both as-grown films are amorphous because of their extremely thin film thickness. The as-grown HfO$_2$ films grown from TDMAH and BTEMAH were crystallized above a critical film thickness of 5 and 8 nm, respectively.[2,9] After annealing at 700 °C, the HfO$_2$ film grown from BTEMAH still remains in an amorphous structure while the HfO$_2$ film grown from TDMAH is fully crystallized at the same temperature. Both films are crystallized by the annealing process at 1000 °C.

Herein, it is worthwhile mentioning that the interfacial layer thickness in the films grown from BTEMAH is thinner than in the films grown from TDMAH at all the annealing temperatures. An interfacial layer can be easily grown on Si substrates by post-annealing at high temperatures due to the diffusion of oxygen atoms through the grown upper-layer. In particular, oxygen diffusion would be accelerated after crystallization because of the high diffusivity along grain boundaries. Indeed, the films grown from TDMAH show a considerable increase in the interfacial layer thickness after annealing at 1000 °C. However, the film grown from BTEMAH shows a quite thin interfacial layer even after annealing at 1000 °C, even though the film is fully crystallized. This tiny increase in the interfacial layer thickness of the HfO$_2$ films grown from BTEMAH could be supported by the higher density of the films as indicated in Fig. 1. The formation of a thick interfacial layer can deteriorate the dielectric properties of the gate oxides due to its low dielectric constant. Therefore, for the purpose of achieving high capacitance, the HfO$_2$ films grown from BTEMAH, which have a thinner interfacial layer, are very promising. After annealing at 1000 °C, indeed, the films grown from BTEMAH exhibit a lower capacitance equivalent thickness (CET) than the films grown from TDMAH at the whole thickness range although the dielectric constants of the HfO$_2$ films grown from BTEMAH and TDMAH, which are calculated from the slope of the graph of the CET-film thickness, are almost identical to each other. This supports that the growth of the interfacial layer is effectively suppressed in the films grown from BTEMAH due to the dense structure of the film.[11] More detailed information on the chemical composition of the interface layers using the X-ray photoelectron spectroscopy and electrical performance was reported previously.[11]

In addition, the dense structure of the films grown from BTEMAH improves the leakage current properties. The leakage current value of the as-grown HfO$_2$ films from BTEMAH is lower than the value of the as-grown HfO$_2$ films from TDMAH. The low leakage current properties of the HfO$_2$ films grown from BTEMAH are maintained even after annealing. These properties may be closely related to the high density of the films. The superior thermal stability of the HfO$_2$ films grown from BTEMAH demonstrates that the heteroleptic hafnium precursor, BTEMAH, is a very promising precursor for the growth of HfO$_2$ films for the application of gate oxides.[11]

It is interesting to note that there is another variation of the TDMAH into a heteroleptic precursor using Cp or the modified Cp ligand.[14] J. Niinistö *et al.*, reported that the replacement of one dimethylamido ligand with the Cp or CpMe ligand increases the ALD temperature

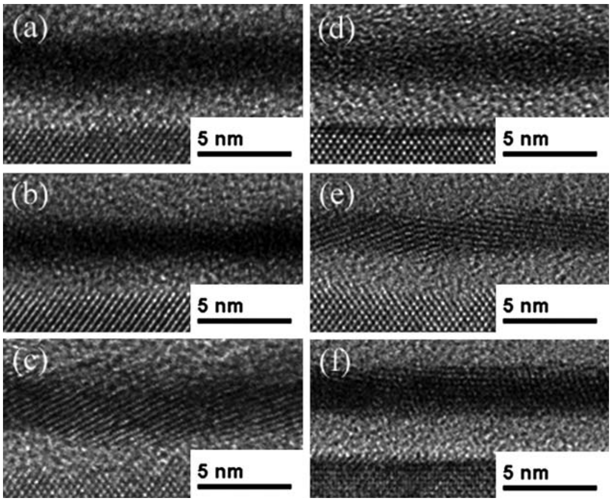

Fig. 2 Cross-sectional HRTEM images of HfO_2 films grown from BTEMAH (a) as-grown at 300 °C and after annealing at (b) 700 °C and (c) 1000 °C. Images (d–f) show HRTEM images of the corresponding films grown from TDMAH. Reproduced from Ref. 11, http://dx.doi.org/10.1039/B806382F. Reproduced by permission of the Royal Society of Chemistry.

window up to ~350 °C, while a higher growth rate (compared to the [$(CpMe)_2HfMe_2$ and $(CpMe)_2Hf(OMe)Me$ precursors]) of 0.07–0.08 nm per cycle was achieved.[14] This is in line with the present work and their former report.[10] The heteroleptic structure of the alkylamido precursor increases the growth rate while the substituted Cp-based ligand retards the thermal decomposition to a higher temperature.[11,14]

It is known that the dielectric constant of HfO_2 is strongly dependent on the crystalline structure. In particular, cubic or tetragonal HfO_2 has a much higher dielectric constant compared to the monoclinic structure.[15] However, the high temperature stable phases, cubic or tetragonal HfO_2 films, are rarely grown by ALD and even CVD. The authors recently reported the formation of tetragonal HfO_2 films on a rutile structured TiO_2 surface using BTEMAH, even without implementing any annealing processes.[12] To investigate the microstructural effect of the under-layer on the crystalline structure of the HfO_2 grown on top, anatase and rutile TiO_2 films, which may have different interfacial energies with HfO_2, were used as substrates. The growth of ALD TiO_2 films with a specific crystalline structure is reported elsewhere.[16,17] Fig. 3(a) shows the change in the CET value of HfO_2/anatase TiO_2/TiN and HfO_2/rutile TiO_2/Ru stacks as a function of the HfO_2 film thickness. The bulk dielectric constant of the HfO_2 films, which could be calculated from the slope of the graph, is 29 and 16 for the films grown on rutile TiO_2 and on anatase TiO_2 under-layers, respectively. The dielectric constant of the HfO_2 films grown on anatase TiO_2 is consistent with the value reported for monoclinic or amorphous HfO_2.[18] However, the high dielectric constant value of the HfO_2 films grown on rutile TiO_2 suggests that the films are not crystallized into a pure monoclinic structure. The smaller CET values of the rutile TiO_2/Ru stack (CET at zero thickness of HfO_2) results from the high dielectric constant (~80) of rutile TiO_2.[16]

The high dielectric constant (29) of the HfO_2 films grown on a rutile TiO_2 under-layer is attributed to the formation of a high temperature stable phase. To further elucidate the crystalline structure of the HfO_2 films grown on a rutile TiO_2 under-layer, the microstructure of the films was observed by HRTEM. Fig. 3(b) shows the cross-sectional HRTEM image of an 8 nm-thick HfO_2/rutile TiO_2 stack film. The film consists of a mixture of amorphous and crystalline structures. It should be noted that a transition thickness for the crystallization of the HfO_2 films grown from the BTEMAH precursor is approximately 18 nm on a Si substrate.[11] Although the thickness of the HfO_2 film in Fig. 3(b) is certainly lower than the transition thickness, some parts of the HfO_2 film were crystallized in the early stages of growth. Indeed, reciprocal lattice analysis using the fast Fourier transformation of the HRTEM images revealed that the crystalline part of the 8 nm-thick HfO_2 film grown on the rutile TiO_2 layer is a tetragonal structure, not a monoclinic structure. On the other hand, the 24 nm-thick HfO_2 film grown on the anatase TiO_2 layer is fully crystallized into a monoclinic structure.[12] This suggests that the rutile TiO_2 surface may effectively reduce the interfacial energy between crystalline HfO_2 grain (high temperature phase) and rutile TiO_2, crystallizing the HfO_2 films into a specific orientation. It was eventually found that the vertices of a two unit cell combined super-cell of tetragonal HfO_2 on a (101) plane could be matched to the vertices of a five unit cell combined super-cell of a rutile TiO_2 (200) plane. On the other hand, a similar lattice match can barely be found between the tetragonal HfO_2 and anatase TiO_2. This suggests that the local epitaxial growth of tetragonal HfO_2 films could be induced on rutile TiO_2 films without forming a randomly oriented monoclinic HfO_2 phase.

Although rutile TiO_2 films have a high dielectric constant of 80, rutile TiO_2 itself is not suitable for a capacitor dielectric in future generation DRAMs due to its relatively inferior leakage properties.[19] This tetragonal HfO_2/rutile TiO_2 stack structure could effectively improve the leakage current properties because tetragonal HfO_2 is a wide band-gap material and has a relatively high dielectric constant. Therefore, the electrical performance of the HfO_2/TiO_2 stacks was examined. Fig. 4(a) shows the current density (J)-applied voltage (V) curves of TiO_2/Ru and HfO_2/TiO_2/Ru films. The J level of the HfO_2/TiO_2 stacks is much lower than the J level of the TiO_2 films, suggesting that the HfO_2 layer on the TiO_2 film is effectively suppressing the leakage current of the stacked capacitor. From the overall summary of the dielectric performance in Fig. 4(b), it is verified that the HfO_2/TiO_2/Ru stack films achieved very low leakage properties even at a CET value smaller than 0.5 nm whereas the J value of the TiO_2/Ru rapidly increased below a CET of 0.8 nm. Consequently, the HfO_2/TiO_2/Ru stack achieved a CET as low as 0.41 nm with a J value of 2×10^{-7} A cm^{-2} at an applied voltage of 0.8 V. This suggests that this

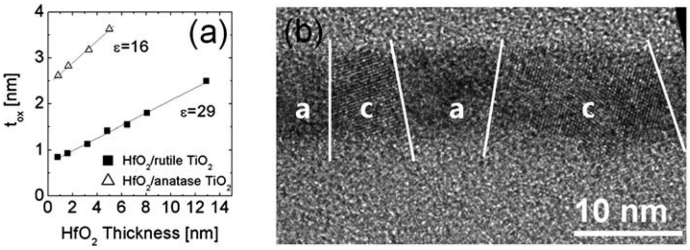

Fig. 3 (a) Change in the CET value of HfO_2/rutile TiO_2 and HfO_2/anatase TiO_2 stacks as a function of the HfO_2 film thickness, (b) cross-sectional HRTEM image of 8 nm-thick HfO_2/rutile TiO_2 stack, which shows a mixed structure of columnar crystalline regions (c) and amorphous regions (a). Reprinted with permission from Ref. 12. Copyright 2010 American Chemical Society.

HfO_2/rutile TiO_2 stack could be a very strong candidate for a capacitor dielectric in next generation DRAM devices. The detailed mechanism for such an improvement in the leakage current performance was reported elsewhere.[20] The primary reason for the leakage current suppression was ascribed to the reduction of defects in the TiO_2 layer occurring during the thin HfO_2 layer deposition. The presence of the thin HfO_2 layer itself has a negligible contribution to the leakage suppression.[20]

In conclusion, a new heteroleptic hafnium precursor, BTEMAH, which was used for the ALD growth of HfO_2 films, achieved a rapid growth rate of 0.16 nm per cycle, the highest ever to be reported for HfO_2 ALD. The film density of the films grown by BTEMAH was also higher than that in conventional reports, and the increase in the interfacial layer on a Si substrate is negligible even after annealing at 1000 °C due to this aspect. In contrast to HfO_2 films grown from TDMAH, the CET value of the HfO_2 films grown from BTEMAH showed a negligible increase up to 1000 °C due to their excellent thermal stability. In addition, the high temperature phase, tetragonal HfO_2, was successfully formed on a rutile TiO_2 substrate even without a post annealing process due to the structural compatibility between the specific planes of tetragonal HfO_2 and rutile TiO_2. The HfO_2 films grown on the rutile TiO_2 under-layer exhibited a high dielectric constant of 29. An extremely low CET of 0.41 nm could be achieved with stable leakage properties from the HfO_2/rutile TiO_2 stacks.

ALD will perform an ever increasing role for growing thin functional layers in future microelectronic devices. The problem of inherent low growth rate in ALD would be compensated for by the innovation of novel precursors and reaction mechanisms. Especially, precursors which show the self-limiting thermal decomposition behavior such as BTEMAH may be utilized to increase the growth rate and to reduce the interfacial layer thickness. Improved reactor design may also contribute to the mass-productivity. The combined layer approach in ALD, as shown in this article, can pave the way to accomplish the required performance which can be hardly met by a single layer.

The heteloptic structure of precursors of several technically relevant metals would provide a viable route to solve several problems related to ALD, such as low growth rate, low deposition temperature, and accompanying low density of the films. However, the more complicated reaction route requires further studies on the growth mechanism perhaps *via in-situ* monitoring tools.

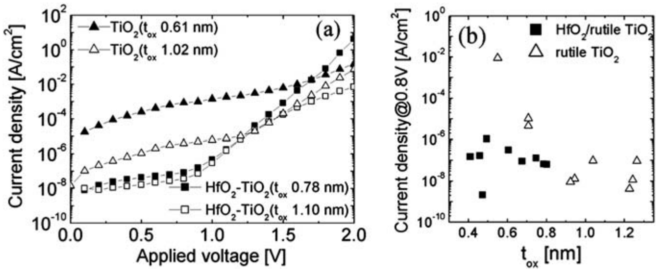

Fig. 4 (a) *J*–*V* curves of TiO_2/Ru and HfO_2/TiO_2/Ru stacks, (b) overall summary of the *J* value at an applied voltage of 0.8 V *versus* CET for TiO_2/Ru and HfO_2/TiO_2/Ru stack films. Reprinted with permission from Ref. 12. Copyright 2010 American Chemical Society.

Acknowledgements

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