Supporting information

Atomic layer deposition of titanium oxide thin film using titanium precursor with a linked amido-cyclopentadienyl ligand

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Bond dissociation energy

Bond dissociation energy (BDE) values were calculated using Equation (1).

$$BDE = D_o^{298K} = \Delta_f H°(A) + \Delta_f H°(B) - \Delta_f H°(AB)$$
(1)

where D_0^{298K} is the enthalpy of the dissociation of the A–B bond, and $\Delta_f H°(A)$, $\Delta_f H°(B)$, and $\Delta_f H°(AB)$ are the enthalpies of the formation of A, B, and AB, respectively. The enthalpies were calculated using Equation (2).

$$H°(298\ K) = E_o + ZPE + H_{translation} + H_{rotation} + H_{vibration} + k_B T$$
(2)

where E_o is the standard total energy of electronic calculations, ZPE is zero-point energy obtained by frequency calculations, and k_B and T are Boltzmann constant and temperature. $H_{translation}$, $H_{rotation}$, and $H_{vibration}$ correspond to the contributions of translation, rotation, and vibration of a molecule, respectively.[1,2] The vibrational frequencies were not scaled because the scale factor (0.9989) was so close to unity that it did not affect the results. All calculations were performed by Materials Studio 7.0 with DMol[3] package (Biovia, USA). The functional theory and basis set were generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) scheme correction and the double numerical polarization (DNP) 4.4.

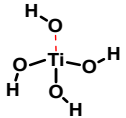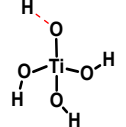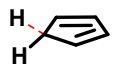Figure S1 shows the BDE values of Ti–O, O–H, N–H, and C–H bonds.
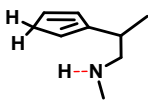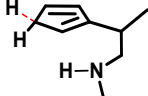
Bonds	Molecular sample	Schematic	BDE (eV)
Ti–O	(OH)$_3$**Ti–OH**		4.72
O–H	(OH)$_3$Ti**O–H**		4.87
N–H	(CH$_3$)$_2$**N–H**		3.87
C–H	**C$_5$H$_5$–H**		3.41
N–H	(C$_5$H$_5$)CH(CH$_3$)(CH$_3$**N–H**)		3.80
C–H	(**C$_5$H$_4$–H**)CH(CH$_3$)(NHCH$_3$)		3.32

Figure S1. BDE values of Ti–O, O–H, N–H, and C–H bonds.

Desorption of byproduct molecules

The desorption of a byproduct molecule, HNMe$_2$ or HCp, from the hydroxylated TiO$_2$ surface was modeled and simulated, as shown in Figure S2. The temperature-dependent free energy of desorption, $G_{des}(T)$ was calculated using Equation (3).

$$G_{des}(T) = (G_{final}(T) + G_{byproduct}(T)) - G_{initial}(T) \qquad (3)$$

where $G_{final}(T)$, $G_{byproduct}(T)$, and $G_{initial}(T)$ are the free energies of surface, gas-phase byproduct molecule, and physisorbed byproduct molecule, respectively. $G_{des}(T)$ under 1 Torr (1 atm = 760 Torr) was calculated using Equation (4).

$$G_{des}(T) \, (1 \, Torr) = G_{des}(T) \, (1 \, atm) + RT\ln P_{byproduct \, molecule} \qquad (4)$$

The free energies were calculated using Equation (5).

$$G(T) = E_o + ZPE + G_{translation} + G_{rotation} + G_{vibration} + k_B T \qquad (5)$$

where $G_{translation}$, $G_{rotation}$, and $G_{vibration}$ correspond to the contributions of translation, rotation, and vibration of a molecule, respectively. The DFT calculation was performed by Materials Studio 7.0 with the DMol^3 package (Biovia, USA). The functional theory of generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) scheme correlation and the basis set of the double numerical polarization (DNP) 4.4 were used in all calculations.

Figure S2 shows the temperature-dependent free energy change for the desorption of $HNMe_2$ or HCp from the TiO_2 surface. The free energy change by the desorption of $HNMe_2$ was negative at 88 °C or higher temperatures. The free energy change by the desorption of HCp was also negative at 184 °C or higher temperatures. The results indicate the spontaneous desorption process of $HNMe_2$ or HCp during the ALD TiO_2 processes.
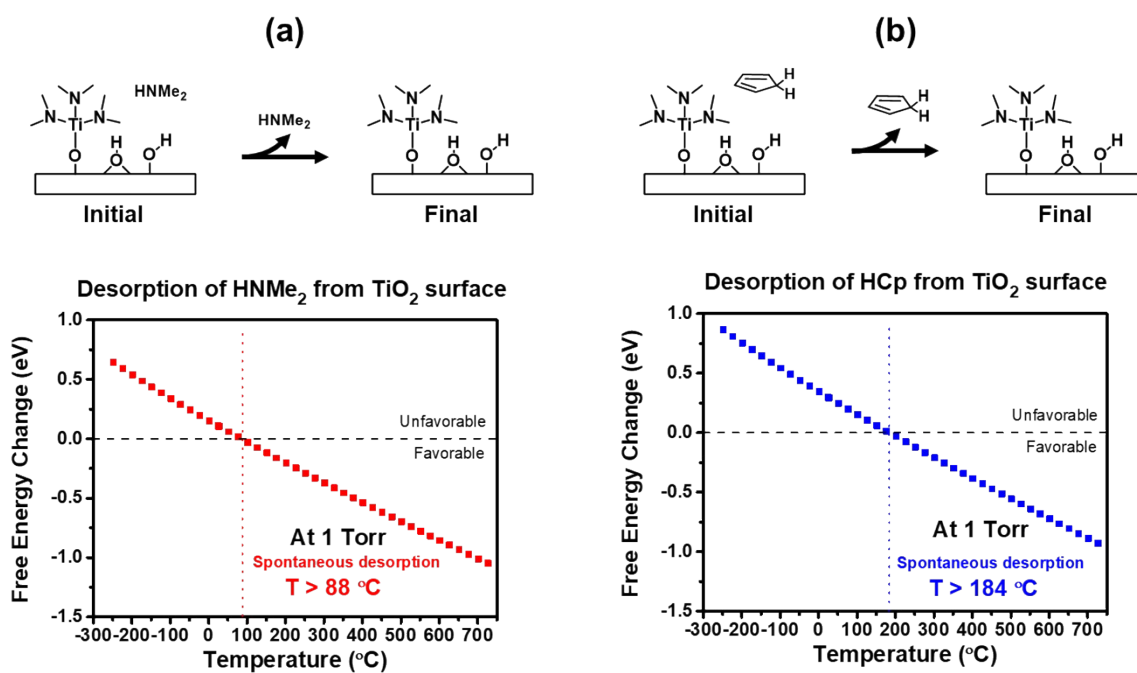

Figure S2. The temperature-dependent free energy change for the desorption of (a) $HNMe_2$ or (b) HCp from the TiO_2 surface.

References:

1   A. K. Chandra and T. Uchimaru, *J. Phys. Chem. A*, 2000, **104**, 9244–9249.

2   S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.*, 2003, **36**, 255–263.