Film growth model of atomic layer deposition for multicomponent thin films

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Atomic layer deposition (ALD) has become an essential technique for fabricating nano-scale thin films in the microelectronics industry, and its applications have been extended to multicomponent thin films, as well as to single metal oxide and nitride films. A mathematical film growth model for ALD is proposed to predict the deposition characteristics of multicomponent thin films grown mainly in the transient regime, where the film thickness varies nonlinearly with the number of cycles. The nonlinear behavior of the growth rate and the composition of multicomponent thin films deposited by ALD depend on the precursor used and adsorbing surface. Hence, the equations to describe the change of surface coverage with precursor adsorption and the surface reaction are derived. The area reduction ratio is introduced as a parameter related to the number of adsorbed precursor molecules per unit area. The proposed model was applied to the deposition of Sr–Ti–O thin films to confirm its validity. SrO and TiO2 films were grown separately to investigate their ALD characteristics and to extract model parameters. As a result, it was shown that the thickness and composition of Sr–Ti–O films follow the trend predicted by the proposed model. © 2005 American Institute of Physics. [DOI: 10.1063/1.1883728]

I. INTRODUCTION

Atomic layer deposition (ALD) for the formation of nano-scale thin films, has received considerable interest because of its inherent ability to achieve high levels of conformity and step coverage, and because it enables precise control of film thickness at atomic dimensions, as a result of self-limited surface reactions. As pointed out in our previous papers, however, in the initial stage of ALD, the number of reactant molecules adsorbing onto the outermost surface changes continuously until the exposed substrate surface is covered with more than one atomic monolayer (ML) of the film to be deposited. This is because the outermost surface onto which the reactant molecules are adsorbed gradually converts from the original substrate to the film that is being deposited. Hence, the growth rate (deposition thickness per cycle) changes continuously with the deposition cycle. As a result, the film thickness no longer follows a linear relationship with the number of deposition cycles. This means that ALD loses its digital thickness controllability, which is one of the most important inherent merits of ALD, in the formation of nano-scale thin films. This initial period is defined as the transient regime, and the following period, where the growth rate remains constant, is called the converged regime. The occurrence of a transient regime is inevitable, since the film to be deposited is composed of a different material from the original substrate. The transient regime makes it more complex to adjust film compositions when the film is composed of multiple components. In ALD, it was thought that film composition can be controlled by the number of deposition cycles allocated to each component using separate sources, instead of a source cocktail. Therefore, as shown in Fig. 1, by adopting the concept of a super-cycle, in which a number of sub-cycles having a number of unit cycles for each component are allocated in sequence, the film composition can be designed and controlled by changing the number of unit cycles dedicated to each sub-cycle. Nevertheless, in real multicomponent ALD, the chemical composition of the outermost surface changes gradually with every unit cycle until the outermost surface is covered with more than one atomic monolayer of the film to be added during a sub-cycle, and the change is repeated periodically in terms of a super-cycle. Therefore, the film growth kinetics using the concept of a super-cycle are dominated by the ALD characteristics originating not from the converged regime, but from the transient regime. As a result, the film composition and film thickness do not follow a linear relationship with the number of unit cycles dedicated to each sub-cycle.

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FIG. 1. Schematic description of the process of multicomponent ALD.
Several models describe the ALD growth transition from nonlinear to linear as a function of the number of cycles. One model is based on the mass balance of reactant chemisorption, and considers reactant size and reaction mode, including ligand exchange and dissociation.\(^6\) This model can predict the growth rate when it is limited by steric hindrance. A model describing the nucleation and growth rate on differently treated substrate surfaces using differential equations has also been proposed.\(^6\) However, these models focus on a single metal oxide, and it is difficult to expand them for application to multicomponent ALD.

This article proposes a film growth model that can predict film growth in the transient regime. This can be used to control film composition and thickness with the number of unit-cycles allocated to each component, and to give guidance in designing super-cycles suitable for multicomponent thin films. The proposed film growth model is used to extract adsorption rate constants and quantities in both the converged and transient regimes; using the extracted adsorption parameters, film growth with a super-cycle can be simulated. To avoid mathematical complexities, here, a steady state in thin films. The proposed film growth model is used to extract information of the surface area occupied by film deposited, For example, \(k\) follows the scheme. “\(p_k/f_{\ell}\)” denotes precursor \(p_k\) chemisorbed on a solid film of \(f_\ell\). As shown in Fig. 1, one super-cycle is composed of several sub-cycles allocated to each precursor, and one sub-cycle comprises a finite number of unit-cycles. A unit-cycle is made up of the sequential pulsing of precursor, purge, reactant, and another purge. The address of a unit-cycle is described by parentheses as \((i,k,j)\), which designates the \(j\)th unit-cycle located in the \(k\)th super-cycle for precursor \(p_k\), which is arranged in the \(i\)th super-cycle. \(\theta^\ell\) is the surface coverage, which denotes the fraction of the surface area covered by a precursor chemisorbed on a given solid film. For example, \(\theta_{p_k/f_\ell}^{i(k,j)}\) is the surface coverage of \(p_k/f_\ell\) in the \((i,k,j)\)th unit-cycle. The surface coverage equals unity when the adsorption of \(p_k\) onto \(f_\ell\) becomes saturated. Moreover, “\(S\)” is the fraction of the surface area occupied by a film exposed to the surface. For example, \(S_{f_\ell}^{i(k,j)}\) is the fraction of the surface area occupied by film \(f_\ell\) after performing the \((i,k,j)\)th unit-cycle.

### II. FILM GROWTH MODEL

#### A. Notations

The notation used in this article is as follows. The letters “\(p\)” and “\(f\)” denote the precursor used and the solid film deposited, respectively. When multiple precursors are used, they are distinguished as \(p_1,p_2,\ldots,p_n\); \(f\) follows the same scheme. “\(p_k/f_{\ell}\)” denotes precursor \(p_k\) chemisorbed on a solid film of \(f_\ell\). As shown in Fig. 1, one super-cycle is composed of several sub-cycles allocated to each precursor, and one sub-cycle comprises a finite number of unit-cycles. A unit-cycle is made up of the sequential pulsing of precursor, purge, reactant, and another purge. The address of a unit-cycle is described by parentheses as \((i,k,j)\), which designates the \(j\)th unit-cycle located in the \(k\)th super-cycle for precursor \(p_k\), which is arranged in the \(i\)th super-cycle. \(\theta^\ell\) is the surface coverage, which denotes the fraction of the surface area covered by a precursor chemisorbed on a given solid film. For example, \(\theta_{p_k/f_\ell}^{i(k,j)}\) is the surface coverage of \(p_k/f_\ell\) in the \((i,k,j)\)th unit-cycle. The surface coverage equals unity when the adsorption of \(p_k\) onto \(f_\ell\) becomes saturated. Moreover, “\(S\)” is the fraction of the surface area occupied by a film exposed to the surface. For example, \(S_{f_\ell}^{i(k,j)}\) is the fraction of the surface area occupied by film \(f_\ell\) after performing the \((i,k,j)\)th unit-cycle.

#### B. Derivation of the model

In ALD, the number of precursor molecules chemisorbed onto the outermost surface increases with the pulse time, and then becomes saturated after reaching a dynamic steady state, which equalizes the adsorption and desorption rates. At saturation, the effective area of \(A_P\) occupied by a precursor molecule chemisorbed on the film surface, which includes not only the physical size of the chemisorbed molecule itself, but also interactions between chemisorbed molecules, can be defined as follows:

\[
A_P = 1/N,
\]

where \(N\) is the number of molecules chemisorbed on the unit surface area at saturation. After the chemisorbed molecules convert into a solid film via chemical reactions with the reactant gas delivered in the following pulse, the effective area \(A_P\) shrinks to the area \(A_f\), which is the real surface area covered by the solid film that is newly formed from an individual chemisorbed molecule. Therefore, the area reduction ratio, \(r\), before and after the chemical reactions can be defined as

\[
r = A_f/A_P.
\]

In general, the area reduction ratio, \(r\), should be less than unity. Furthermore, \(r\) is not a constant, but is a variable that depends on the outermost surface, as the number of molecules chemisorbed on a solid surface should depend on the material constituting the outermost surface, and also depend on the precursors used. Therefore, the area reduction ratio is denoted as \(r_{p_k/f_\ell}\), when a precursor of \(p_k\) chemisorbed on a solid film of \(f_\ell\) is converted into a solid film \(f_k\).

Using this concept of area reduction ratio, it is possible to derive equations describing the characteristics of film growth in ALD, including both the transient and converged regimes. When \(n\) kinds of precursor \((p_1,p_2,\ldots,p_n)\) are used to deposit a solid film composed of \(n\) metal components, the outermost surface is generally composed of \(n\) kinds of solid film \((f_1,f_2,\ldots,f_n)\) during film deposition. The status of the outermost surface before precursor injection in the \((i,k,j)\)th unit-cycle is shown in Fig. 2(a). In reality, the surface does not consist of blocks of each film, but it is presented schematically in this way to show the principle. During precursor injection, precursor \(p_k\) can be chemisorbed on outermost surfaces of all kinds. The coverage of chemisorbed precursor \(p_k\) in a unit area is obtained by summing the coverage of chemisorbed precursor on each surface, as shown in Fig. 2(b). Therefore, after injecting precursor \(p_k\), the coverage of precursor \(p_k\) can be denoted as:

\[
\theta_{p_k/f_\ell}^{i(k,j)} = \theta_{p_k/f_\ell}^{i(k,j)}(j,k,j-1) + \cdots + \theta_{p_k/f_\ell}^{i(k,j)}(j,k,j-1)
\]

\[
= \sum_{\ell=1}^{N} \theta_{p_k/f_\ell}^{i(k,j)}(j,k,j-1).
\]

This finite summation has a value between 0 and 1. At saturation, \(\theta_{p_k/f_\ell}^{i(k,j)} = 1\) for all \(\ell\), then

\[
\theta_{p_k/f_\ell}^{i(k,j)} = \sum_{\ell=1}^{N} (j,k,j-1) = 1.
\]
FIG. 2. Schematic diagram showing the changes in the fraction of surface area covered by solid films and precursors for each step of the (i, k, j)th unit cycle: (a) Before injecting metal precursor \( p_s \), (b) after chemisorption of the metal precursor \( p_s \), (c) after conversion of metal precursor \( p_s \). The newly formed surface area resulting from the chemical reaction between precursor molecules of \( p_s \) and surface that was covered with the precursor molecules is partially revealed after the chemical reaction of precursor \( p_s \) chemisorbed on solid film \( f_s \). At saturation, Eq. (5) can be expressed as a form of a recursive equation

\[
S_{f_k}^{(i,k,j)} = \sum_{\ell=1}^{n} r_{p_{df}/f_s} S_{f_s}^{(i,k,j-1)} + (1 - r_{p_{df}/f_s}) S_{f_k}^{(i,k,j-1)},
\]

where \( r_{p_{df}/f_s} \) is the area reduction ratio for precursor \( p_s \) chemisorbed on film surface \( f_s \). The first term on the right-hand side of Eq. (5) is the fraction of newly formed solid film \( f_k \) in the \((i,k,j)\)th unit cycle and the second term is the fraction of revealed solid film \( f_k \) as a result of surface area shrinkage. Consequently, the fraction of the surfaces other than \( f_k \) can be written as

\[
S_{f_k}^{(i,k,j)} = (1 - r_{p_{df}/f_s}) S_{f_s}^{(i,k,j-1)} \quad \ell = 1, \ldots, n \text{ and } \ell \neq k.
\]

Moreover, the fraction of the surface area equals one. Then, the thickness of the deposited film is obtained by multiplying the newly formed surface area by the monolayer thickness. Therefore, when \( n \) kinds of precursors are used to deposit a multicomponent thin film, film growth during one super-cycle is represented by

\[
\text{Growth rate (thickness/super-cycle)} = \sum_{k=1}^{n} \left( \sum_{j=1}^{J_k} \frac{r_{p_{df}/f_s}}{A_f} S_{f_s}^{(i,k,j)} \right).
\]

where \( h_{f_k} \) is the monolayer thickness of solid film \( f_k \).

In Eq. (8), the number of metal atoms deposited during the sub-cycle by \( p_s \) can be obtained by dividing the fraction by \( A_f \), which is the surface area occupied after one \( p_s \) molecule is converted into a solid film of \( f_s \). Consequently, the composition of elements \( c_m \) can be calculated as:

\[
c_m = \sum_{j=1}^{J_m} \sum_{\ell=1}^{n} \left( \frac{r_{p_{df}/f_s}}{A_{f}} S_{f_s}^{(i,m,j-1)} / A_{f,m} \right),
\]

\[
S_{f_k}^{(i,k,j)} = \left( \frac{1}{r_{p_{df}/f_s}} \right) S_{f_s}^{(i,k,j-1)} + \ldots + \left( \frac{1}{r_{p_{df}/f_s}} \right) S_{f_s}^{(i,k,j-1)} + \ldots + \left( \frac{1}{r_{p_{df}/f_s}} \right) S_{f_s}^{(i,k,j-1)}
\]

\[
= \sum_{\ell=1}^{n} r_{p_{df}/f_s} S_{f_s}^{(i,k,j-1)} + (1 - r_{p_{df}/f_s}) S_{f_k}^{(i,k,j-1)}.
\]
FIG. 3. Simulated thickness as a function of the number of cycles with respect to the various area reduction ratios. (i) \( r_{f_2}/r_{i_1}=0.5 \), (ii) \( r_{f_2}/r_{i_1}=0.06 \), (iii) \( r_{f_2}/r_{i_1}=0.7 \), (iv) \( r_{f_2}/r_{i_1}=1.7 \), and (v) \( r_{f_2}/r_{i_1}=1.0 \).

sequence using \((i, k, j)\) can be simplified as \((j)\) by omitting \(i\) and \(k\). In addition, Eqs. (6), (7), and (9) can be simplified as:

\[
S_{f_1}^{(j)} = r_{f_2}/r_{i_1} S_{f_2}^{(j-1)} + S_{f_1}^{(j-1)} (1 - r_{f_2}/r_{i_1}) S_{i_1}^{(j-1)}
\]

\[
= S_{f_1}^{(j-1)} + r_{f_2}/r_{i_1} S_{f_2}^{(j-1)},
\]

\[
S_{f_2}^{(j)} = (1 - r_{f_2}/r_{i_1}) S_{f_2}^{(j-1)}.
\]

Growth rate (thickness/cycle) = \( h_{f_1} (r_{f_2}/r_{i_1}) S_{f_1}^{(j-1)} + r_{f_2}/r_{i_1} S_{f_2}^{(j-1)} \),

where \( S_{f_1}^{(j)} \) and \( S_{f_2}^{(j)} \) is the fraction of the surface area occupied by solid films \( f_1 \) and \( f_2 \) on the outermost surface after the \( j \)th cycle, respectively. \( h_{f_1} \) is the monolayer thickness of the solid film \( f_1 \). This system has initial conditions \( S_{f_1}^{(0)} = 0 \) and \( S_{f_2}^{(0)} = 1 \). In addition, \( S_{f_1}^{(j)} + S_{f_2}^{(j)} = 1 \) must always be satisfied. After several cycles have proceeded, \( S_{f_2}^{(j)} \) converges on 0 and \( S_{f_1}^{(j)} \) becomes unity. Then, the growth rate equals \( h_{f_1} r_{f_2}/r_{i_1} \). This means that the growth rate is constant if \( r_{f_2}/r_{i_1} \) can be extracted from the data in the converged region.

Figure 3 plots thickness as a function of the number of cycles, with respect to the area reduction ratios of a metal precursor on the surfaces of the original substrate. If \( r_{f_2}/r_{i_1} \) \( \geq 1 \) [case (iii)], the growth rate becomes \( h_{f_1} r_{f_2}/r_{i_1} \) from Eq. (13), which is independent of the number of cycles. The graph of thickness as a function of the number of cycles will be a straight line passing through the origin. If \( r_{f_2}/r_{i_1} < 1 \) for cases (i) and (ii), the linear (or converged) regime of the curves is shifted down from the straight line for case (iii). Conversely, in cases (iv) and (v), for which \( r_{f_2}/r_{i_1} > r_{f_2}/r_{i_1} \), the graphs are shifted upward. Therefore, the area reduction ratio of a metal precursor on different materials with a deposited film can be obtained by fitting the experimental data to the model.

III. APPLICATION OF THE PROPOSED MODEL TO THE SR–TI–O SYSTEM

This model was applied to the deposition of a SrTiO\(_3\) thin film using bis(dipivaloylmethanoato)strontium [Sr(DPM)\(_2\)] and titanium tetraisopropoxide [TTIP, Ti(OC\(_3\)H\(_7\))\(_4\)], diluted to respective concentrations of 0.2 and 0.4 M in n-butyl acetate, as the metal precursors. These were injected into the vaporizer using a liquid delivery system with an Ar and O\(_2\) gas mixture as the carrier and purge gases. This Ar–O\(_2\) gas mixture was also used as the reactant to generate rf plasma, which was applied directly over the wafer. The SrO and TiO\(_2\) films were deposited at a growth temperature of 275 °C and a total pressure of 3 Torr. Film thickness was measured with an ellipsometer and the composition and depth profiles were analyzed using auger electron spectroscopy (AES). The composition of each element obtained from AES was corrected using a SrTiO\(_3\) single crystal in the (100) orientation.

The growth of SrO and TiO\(_2\) films was investigated to confirm the self-limited growth mechanism typical of ALD (not shown here). The growth rate was independent of the precursor injection time, post-precursor purge time, and plasma time. This implies that the adsorption of metal precursors was saturated and conversion of all the chemisorbed molecules into the solid film was achieved. Therefore, deposition was performed under the saturated growth condition.

To apply this model to SrTiO\(_3\) deposition, four area reduction ratios are needed: \( r_{Sr(DPM)/SrO} \), \( r_{TTIP/TiO_2} \), \( r_{Sr(DPM)/TiO_2} \), and \( r_{TTIP/SrO} \). Therefore, as described in the parameter extraction method, SrO and TiO\(_2\) films were deposited on TiO\(_2\) and SrO substrates, respectively, as a function of the number of cycles (Fig. 4). The linear fits of the experimental data are represented by the solid and dotted lines. The slopes of the two lines are 0.55 and 0.35 Å/cycle. The monolayer thicknesses of SrO and TiO\(_2\) film were obtained from the Rutherford backscattering spectrometry (RBS) analysis. The densities of the SrO and TiO\(_2\) films were \( 3.6 \times 10^{22} \) and \( 3.11 \times 10^{22} \) molecules/cm\(^3\), respectively. The calculated average distances between Sr and Ti atoms were 3.1 and 3.18 Å, respectively. These distances can be considered the thickness of 1 ML film. Therefore, \( r_{Sr(DPM)/SrO} \) and \( r_{TTIP/TiO_2} \) are 0.18 and 0.11, respectively. In addition, since both lines are shifted downward, as shown in the inset of Fig. 4, less Sr(DPM)\(_2\) is chemisorbed on the TiO\(_2\) surface than on the SrO surface, and TTIP behaves similarly to Sr(DPM)\(_2\). This result is in good agreement with the result of Rahlu et al.\(^8\). The values of \( r_{Sr(DPM)/TiO_2} \) and \( r_{TTIP/SrO} \) obtained using a computer program with a numerically iterative method are 0.05 (±0.27) and 0.09 (±0.83) respectively.

To verify the validity of the proposed model and ex-
extracted parameters, the deposition characteristics of Sr–Ti–O films were compared with the simulation result obtained using this model. The number of unit cycles in a sub-cycle of Sr(DPM)$_2$ (namely, the number of SrO unit cycles) was fixed at one, while the number of TiO$_2$ unit cycles was varied from 1 to 5. Figure 5 shows the variation in the growth rate and Ti composition as a function of the number of TiO$_2$ unit cycles. Using the obtained parameters above, the growth rate and composition were predicted from Eqs. (9) and (10). As expected, the Ti composition approached the value of 1 and the growth rate gradually increased with the number of TiO$_2$ unit cycles. Both the experimental growth rate and composition were in good agreement with the prediction of our model, while there were significant differences between the experimental data and a simple calculation using data from the converged regime of SrO and TiO$_2$ ALD without considering the transient regime.

IV. CONCLUSIONS

A mathematical film growth model and a process for multicomponent thin film ALD were proposed. To evaluate the amount of chemisorbed precursor molecules on surfaces, the concept of area reduction ratio was introduced and an experimental extraction method was suggested. This model was applied to the deposition of SrTiO$_3$ thin film. The amount of Sr(DPM)$_2$ adsorption on a TiO$_2$ surface was about 27% of that on an SrO surface, while it was about 83% for a TiO$_2$ surface. A stoichiometric SrTiO$_3$ film was successfully deposited and its thickness and composition agreed well with the model predictions.

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