The Characteristic of TMG adsorption on the Si(100)(2×1) surface in atomic layer deposition (ALD): Computational prediction of $Si_9H_{12}O_2GaCH_3$ structure

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ABSTRACT

This work reports the adsorption characteristic of trimethylgallium (TMG) on the silicon surface in the adsorption step of atomic layer deposition (ALD) to prepare gallium oxide thin film by using TMG as the gallium source. One dimer Si(100)(2×1) is employed as the substrate for the TMG adsorption, since the surface hydroxyls are utilized as the absorption sites. TMG is predicted to consume the two sites adsorption on the top surface of silicon substrate. The adsorption characteristic on the silicon surface and the molecule vibrations are calculated by Gaussian09 package for standard method with B3LYP/6-311G**. The adsorption pressure is controlled at the constant of 8.6×10^{-3} torr, while the process temperatures are varied. The Gibbs free energy value is used to consider as self-adsorption on the silicon substrate. The results showed that TMG is possible to adsorb on the silicon surface with two sites adsorption as the $Si_9H_{12}O_2GaCH_3$ structure at the process temperature is rising to ~266.14 °C. Besides that, the adsorption characteristic and the vibrational frequencies of $Si_9H_{12}O_2GaCH_3$ surface structure are also reported in this paper.

Keywords: Atomic layer deposition (ALD), TMG adsorption, Si(100)(2×1), Gallium oxide, Computational method

INTRODUCTION

The varieties of oxide thin film technology are expected to use for many applications such as hard coating (Figueiredo et al., 2015), decorative coating (Chena et al., 2014), electronics coating (Mohammeda et al., 2018), medical devices coating (Nakonieczny et al., 2017), and functional coating (DharPurkayastha et al., 2014). Even though, there are many conventional deposition methods can be employed to prepare the thin film on the various substrates, such as the chemical vapor deposition method (CVD) (Jeong et al., 2018), the physical vapor deposition method (PVD) (Serpini et al., 2017), and atomic layer deposition (ALD) (Pansila et

Article history:
Received 13 June 2018; Received in revised form 11 January 2019;
Accepted 27 June 2019; Available online 27 December 2019

al., 2015), but the thickness uniformity on the complicated surface with large surface might be required in near future especially for the flexible electronics.

For the case of chemical vapor deposition (CVD) method, it is convenient to prepare thin film surface on the large surface area or the substrate with high process temperature that cause to consume much of thermal budget. CVD method does not allow for the substrate that easy to melt at high process temperature. Due to high temperature, it is effectiveness in the physical properties of the substrate such as for flexible substrate or plastic devices. In the case of the physical vapor deposition (PVD) like a sputtering method, it is possible to deposit the film layer on some area on the substrate surface, but it does not allow for the uniform surface thickness in large area of substrate. In order to achieve the good thickness uniformity and controllability of the thickness of the film on an atomic scale, *atomic layer deposition (ALD)* method should be realized for taking a consideration.

The ALD is considering for the high quality of the film on complicated substrate with large area for devices. It can also deposit the ultra-thin film with the conformal surface and small roughness. The ALD method is the deposition technique of thin film that performs by repeating saturated adsorption of gas source onto the substrate and its reactivation with the highly reactive gases. A layer of the film is obtained after one cycle of ALD process. One cycle of the ALD consists of four steps, such that, 1) precursor adsorption, 2) evacuation, 3) reaction with reactive gas, and 4) evacuation, the processes are being performed respectively (Pansila et al., 2015). ALD method is considered for an excellent method to prepare a smooth and uniform thin film. Especially on small and large complicated surface areas. The ultra-thin film deposition with an atomic-scale thickness controllability can be obtained by using this method. The precise thickness of the film can be controlled by counting the cycle numbers. ALD can deposit with very small thickness of thin film with the conformal surface on the complicated substrates, and either on the plastic substrates (Tsai et al., 2015). Besides that, ALD is possible to deposit the film at *low temperature* as well. So as to investigate the optimal condition in ALD process, the adsorption steps in the ALD must be rigorously studied. The adsorption characteristic of the precursor on a substrate is very important to understand. That includes the number of the consuming adsorption site on the substrate surface and the initial process temperature in which the surface reaction has appeared. We have to investigate that the temperature effect to activate the self-surface adsorption of precursor. If the precursor cannot adsorb on the substrate, then the ALD process is impossible to perform.

In this paper, we report the TMG adsorption on one Si-dimer (100)(2×1) surface with two-site adsorption to study the adsorption characteristic of TMG in the gallium oxide ALD process. TMG is used as the Ga source due to high reactivation with the hydroxyl group. Moreover, the production gases from the TMG adsorbed surface in the reaction process is not toxic to the nature. Silicon is used as a substrate, because of its highly reactive surface (Smedarchina et al., 2003). In this work, the $Si_9H_{12}O_2GaCH_3$ structure is focused for investigation. The Avogadro

platform is employed to visualize the molecular design (Hanwell et al., 2012). The characteristic of surface adsorption, the Gibbs free energy value, and the vibrational frequency of hydrocarbon in TMG adsorption on the two-site hydroxylated silicon surface by various process temperatures are calculated by the Gaussian09 software package (Frisch et al., 2010).

SURFACE ADSORPTION AND COMPUTATIONAL METHOD

As aforementioned, we introduced the important process in the first-half ALD cycle as adsorption steps of the precursor in ALD process. In this section, we show the basic model for 1 cycle in ALD process in Figure 1. One cycle in ALD process is including of the precursor surface, the evacuation of residual gas, the reaction with highly reactive species, and the evacuation of the by production (Pansila et al., 2015). In this work, we study the TMG adsorption on the one dimer of Si(100)(2×1) with the $Si_9H_{12}O_2GaCH_3$ structure by using hydroxylate surface ($–OH_{(surface\ species)}$) as the adsorption sites. The characteristic of TMG adsorbed silicon surface and calculation of vibrational frequencies of TMG adsorbed Si(100) surface at the different temperatures are investigated by the Gaussian09 software package. By using Becke, three-parameter, Lee-Yang-Parr (B3LYP) method with standard 6-311G(d, p) basis set. The Gibbs free energy value is considering to evaluate the initial process temperature in adsorption steps. TMG ($Ga(CH_3)_3$) in the gas phase is used as a Gallium source. One dimer of Si(100)(2×1) is used as being the substrate (Figure 3a). To produce the surface adsorption site, the silicon surface is treated by the hydroxyl radicals (OH^-) in gas phase to replace the hydrogen-occupation as silicon hydride (Si–H) on the top surface of silicon dimer, in order to produce the Si–OH surface adsorption site (Figure 3b). The $Si–OH_{(surface)}$ adsorption sites are optimized and evaluated the vibrational mode as shown in Figure 3c. The TMG gas is irradiated to consume the –OH adsorption sites on the top surface of Si-dimer with two-site adsorption (Figure 4a). The characteristics of the surface adsorption of $Si_9H_{12}O_2GaCH_3$ structure are studied by using Gaussian09 software package and B3LYP method (Figure 4b). The vibrational frequencies and the Gibbs free energy value are also calculated. The scaling factor of 0.961 is applied to correct the vibrational frequencies of hydrocarbon in the TMG adsorbed surface.

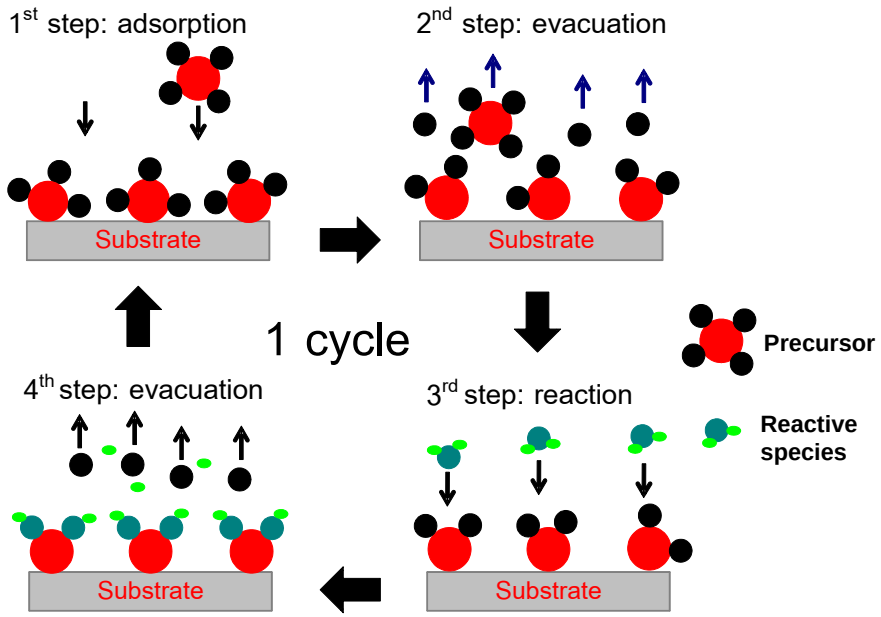


Figure 1 Basic model for 1 cycle in ALD process

RESULTS AND DISCUSSION

TMG ADSORPTION ON Si(100)(2×1)

This work employed TMG gas phase as gallium source. The molecule of TMG includes one gallium atom and three molecules of methyl as $Ga(CH_3)_3$ (Jensen, 2004). The Si_9H_{14} structure is used as the substrate for the TMG adsorption (Figure 3a) (Santos et al., 2005). The –OH adsorption site is produced by hydroxyl radical. It can be prepared from the water-vapor-plasma (Figure 3b). Because of its highly reactive hydroxyl radical then it can be replaced by two-hydrogen atom in the double occupy dimer (H–Si–Si–H) on the top layer of Si(100) as shown in Figure 3c.

The hydrogen atom is used to compensate the valence electrons and restricted geometry, to correct the simulations for Si one dimer. The characteristic of $Si_9H_{12}(OH)_2$ structure have been reported by Ren (2009). The strongly vibrational frequencies of $H–O_{(1)}Si_{(1)}$ and $Si_{(2)}O_{(2)}–H$ are calculated of 3684.45 and 3709.67cm^{-1}, which is corresponding to the stretching vibrational mode. While the vibrational bending mode of 898.23, 843.61, and 800.80 cm^{-1} are given from both of the O–H surface structure (Sukhasena and Pansila, 2014).

In this section, we shall discuss the adsorption step of TMG in gallium oxide ALD for the $Si_9H_{12}O_2GaCH_3$ structure. The adsorption step is importance in the ALD process. Since the TMG gas is exposed to the HO–Si–Si–OH adsorption sites, as shown in Figure 4a. There was reported that TMG requires the two-site adsorptions (Pansila et al., 2015).

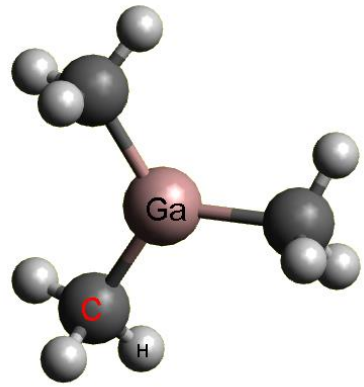
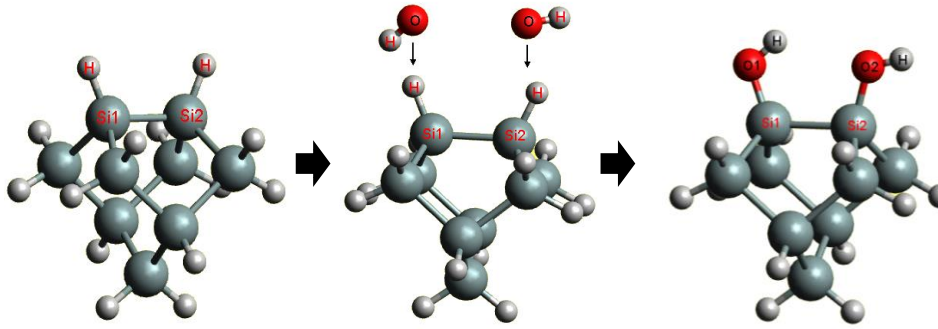


Figure 2 Trimethylgallium (TMG) molecule.



(a) Si(100) substrate (Si_9H_{14}) (b) OH^- radical treated Si_9H_{14} (c) Si–OH adsorption site

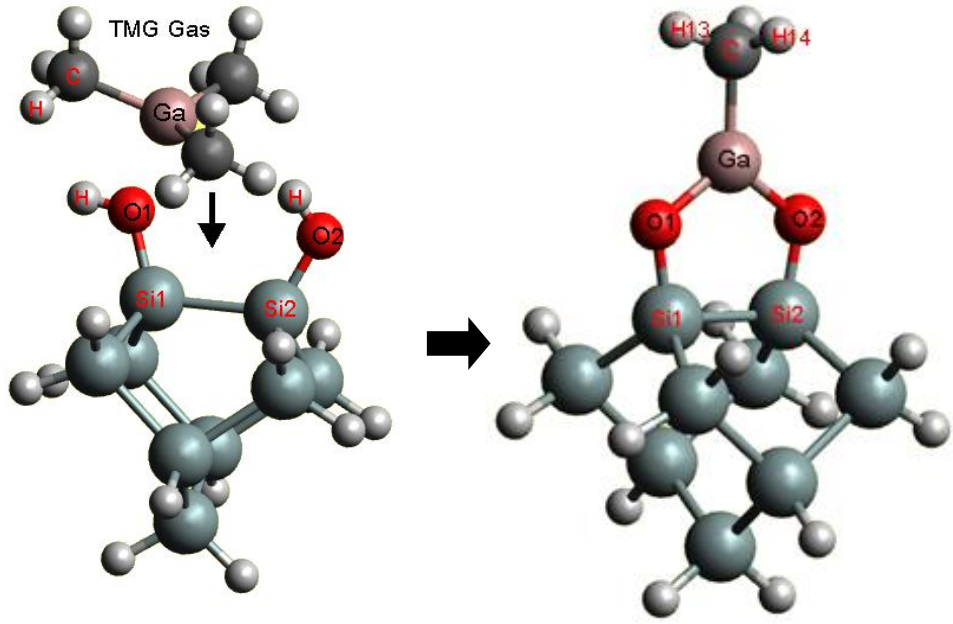
Figure 3 Production process of surface adsorption site in ALD.

In this work, we assume that two $–CH_3$ molecules break from $Ga(CH_3)_3$ molecule, since TMG gas is irradiated in the ultra-high vacuum system. The residual of $–GaCH_3$ molecule move to occupy the $Si–OH_{(surface)}$ adsorption site with two-site adsorption. Then the process produces the $Si_9H_{12}O_2–Ga–CH_3$ surface structure. In this step, the Gaussian calculation that using B3LYP method gives the optimized geometry as shown in Figure 4b. The adsorption characteristics obtained from the Gaussian calculation are also reported in this paper. The bonding length in $Si_{(1)}–O_{(1)}GaCH_3$ and $Si_{(2)}–O_{(2)}GaCH_3$ are 1.689 and 1.688 Å, respectively. The triangle between $Si_{(1)}–O_{(1)}–GaCH_3$ and $Si_{(2)}–O_{(2)}–GaCH_3$ are 115.9˚ and 115.8˚, respectively. The triangle between $O_{(1)}–Ga–O_{(2)}$ is 108.6˚, while the bonding length in $O_{(1)}–GaCH_3$ and $O_{(2)}–GaCH_3$ are 1.830 and 1.831 Å, respectively. The distance

between Ga–C atom is 1.950 Å. Even though, the calculation gives the information of the adsorption characteristic of TMG adsorbed two-site adsorptions, we should investigate the atomic vibration of C–H in TMG molecule that correspond to the infrared region (IR) in order to confirm the existence of TMG adsorption on the silicon surface for experimental step. The IR adsorption spectroscopy (IRAS) with silicon prism can be helped to investigate the existence of TMG on the surface (Pansila et al., 2015). Here, we shall report the atomic vibration of C–H in TMG adsorbed the top layer of Si–dimer, which is calculated by Gaussian09 and scaling of 0.9610 to correct the frequencies in the IR region. The strong vibration of $–CH_3$ molecule in the IR region is only reported in this paper. Next is to consider the adsorbed molecule of methyl in $–GaCH_3$ adsorption, which includes the atoms of C, $H_{(13)}$, $H_{(14)}$, and $H_{(15)}$. The calculation gives the vibrational frequencies of 2948.2 and 3030.9 cm^{-1} that are contributed to the asymmetric stretching mode. While vibrational frequencies of 3046.79 cm^{-1} is contributed to the asymmetric stretching mode. The vibration frequencies of 1210.81, 1410.7, and 1411.86 cm^{-1} are contributed to bending vibrational mode.

To consider the effect of the process temperature on the TMG adsorbed silicon surface in the adsorption step, the Gibbs free energy value should be realized. The process temperature ranges from 160 to 350 °C are varied, since the adsorption pressure is kept at the constant of 8.6×10^{-3} torr. From the calculation, we found that the Gibbs free energy is the negative value when the process temperature is rising to 266.135 °C. By the second's law of thermodynamics, the reaction will be appeared if the Gibbs free energy is the negative value, which is the effect of additional temperature. Table 1 shows the Gibbs free energy values according to process temperatures. This indicates that two-sites-adsorption structure will be occurred when the process temperature is higher than that of 266.00 °C.

We can see the Gibbs free energy to become the negative value if the process temperature rises to ~266.135 °C. This might indicates that TMG begins adsorption on silicon surface as the $Si_9H_{12}O_2–GaCH_3$ structure in adsorption step. We discuss here that TMG is possible to exist on silicon at the temperature exceeds ~266.130 °C. We propose the possible chart of the relationship between the process temperature and the Gibbs free energy value as shown in Figure 5. We can see that the Gibbs free energy is in a negative zone if the temperature is higher than ~266.130 °C. This indicates that the $Si_9H_{12}O_2GaCH_3$ structure possible to exist at the temperature is higher than 266.130 °C. To discuss this phenomenon, we assume that $–CH_3$ is easier to dissociate from TMG molecule at high temperature in which the higher temperature prevents the $–CH_3$ adsorbed surface. That is advantageous to increase the thickness and the density of the gallium oxide film.



(a) Si_9H_{12}–$(OH)_2$ surface (b) $Si_9H_{12}O_2GaCH_3$

Figure 4 The possibility of TMG adsorption on the silicon surface as $Si_9H_{12}O_2GaCH_3$.

Table 1 The process temperature and the Gibbs free energy value with the constant adsorption pressure of 8.6×10^{-3} torr.

Temperature (°C)	Gibbs free energy (Hartree)
160.0000	0.0398000
250.0000	0.0063000
266.0000	0.0000540
266.1250	0.0000040
266.1300	0.0000020
266.1350	-0.0000009
266.1375	-0.0000010
266.1400	-0.0000020
266.2500	-0.0000450
266.5000	-0.0001430
280.0000	-0.0054200
350.0000	-0.0340000

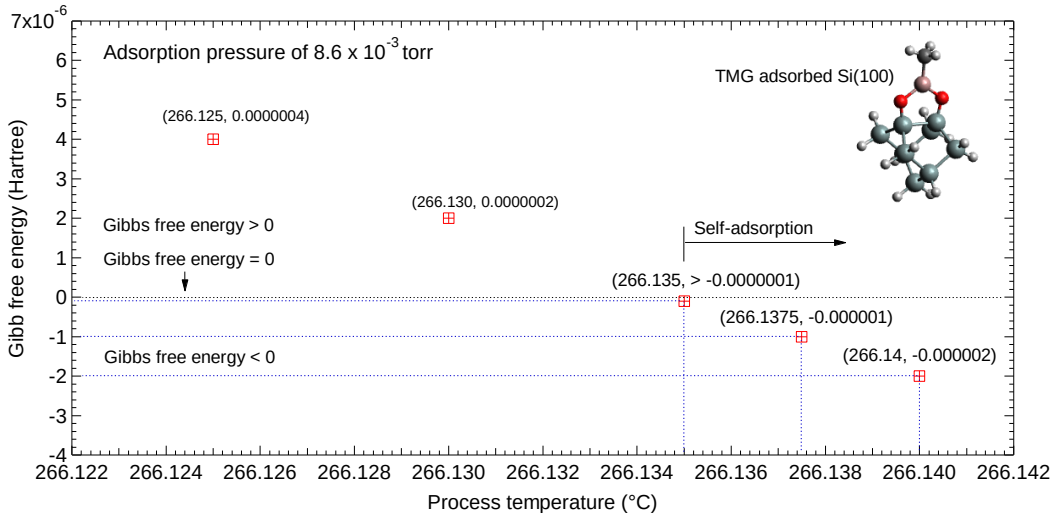


Figure 5 The possible chart of the relationship between process temperature and Gibbs free energy.

CONCLUSIONS

The Gaussian calculation helpfully uses to calculate the adsorption characteristic of the TMG adsorption on the Si(100)(2×1) surface in the thermal ALD process by various temperatures. The calculation indicates that TMG is possible to adsorb on the silicon top-surface with the $Si_9H_{12}O_2GaCH_3$ structure at the process temperature is higher than 266.130 °C. The obtained vibrational frequency of TMG adsorbed silicon surface from the calculation has the benefit to be used as the theoretical frequency to refer to the experimental work. Base on the computational calculation, we assume that the thermal ALD by using TMG as gallium source with two- site adsorption might be improved the thickness and the density of gallium oxide film. It is convenience to predict the reaction mechanism in the atomic layer deposition process by performing the computational work before designing the experiments.

ACKNOWLEDGMENTS

This work was partly supported by Research Grant from Faculty of Science at Sriracha, Kasetsart University.

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