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Surface Chemistry of Ga(CH₃)₃ on Pd(111) and Effect of Pre-covered H and O

Liang-bing Ding, Yun-sheng Ma*, Jie Hu, Bo-hao Chen

Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China.

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The adsorption and decomposition of trimethylgallium (Ga(CH₃)₃, TMG) on Pd(111) and the effect of pre-covered H and O were studied by temperature programmed desorption spectroscopy and X-ray photoelectron spectroscopy. TMG adsorbs dissociatively at 140 K and the surface is covered by a mixture of Ga(CH₃)_x ($x=1, 2$ or 3) and CH_x(a) ($x=1, 2$ or 3) species. During the heating process, the decomposition of Ga(CH₃)₃ on clean Pd(111) follows a progressive Ga–C bond cleavage process with CH₄ and H₂ as the desorption products. The desorption of Ga-containing molecules (probably GaCH₃) is also identified in the temperature range of 275–325 K. At higher annealing temperature, carbon deposits and metallic Ga are left on the surface and start to diffuse into the bulk of the substrate. The presence of precovered H(a) and O(a) has a significant effect on the adsorption and decomposition behavior of TMG. When the surface is pre-covered by saturated H₂, CH₄, and H₂ desorptions are mainly observed at ~315 K, which is ascribed to the dissociation of GaCH₃ intermediate. In the case of O-precovered surface, the dissociation mostly occurs at ~258 K, of which a Pd–O–Ga(CH₃)₂ structure is assumed to be the precursor. The presented results may provide some insights into the mechanism of surface reaction during the film deposition by using trimethylgallium as precursor.

Key words: Ga(CH₃)₃, Pd(111), Adsorption, Decomposition, X-ray photoelectron spectroscopy, Temperature programmed desorption spectroscopy

I. INTRODUCTION

Recent progresses have been made progressively in the synthesis of solid thin film with atomic control in thickness and conformal structure by using atomic layer deposition techniques [1, 2]. Generally, the overall reaction involved in atomic layer deposition process can be divided into two self-limiting surface reactions occurring in a sequential fashion [1, 2]. In a recent perspective, it has been pointed out that several problems often have been overcome to obtain a clean, high-quality film by atomic layer deposition method, including the suppression of impurity, the control of the stoichiometry, the role of specific surface sites *etc.* [2]. Therefore, the surface chemistry involved in atomic layer deposition process needs to be better understood at a molecular level.

Ga-based materials such as Ga₂O₃, GaAs, and GaN have been utilized in a variety of applications such as light emitting diodes, gas sensors, electronics, and transparent conducting oxides [1, 3, 4]. Trimethylgallium (TMG) has been widely used as an important organometallic precursor in film deposition tech-

niques such as molecular beam epitaxy, metal-organic chemical vapor deposition and atomic layer epitaxy. For example, a recent investigation reported that high-quality Ga₂O₃ thin films have been prepared successfully utilizing TMG and ozone [4]. It is necessary to get a better understanding in the surface chemistry of Ga-containing precursors such as TMG on metal/semiconductor substrate.

Generally, the reaction and dissociation of TMG shows a complicated pattern on various substrates [4–14]. Previous studies indicate that the adsorption and reaction of TMG is dependent on the orientation of Si substrates [13, 14]. On Si(111), TMG adsorbs mainly molecularly at room temperature as well as a small part of TMG dissociation resulting in –CH₃ groups bonded the Si substrate [14]. Several desorption products were observed in the TDS results: the desorption of TMG occurred at 423–473 K, C₂H₄, CH₄, and CH₃ desorbed at 423–623 K, GaCH₃ desorption at 473–723 K and H₂ desorption at 773 K [14]. In contrast, only CH₄ and H₂ were detected as decomposition products on Si(100), without the formation of C₂H₄ and Ga(CH₃) although a similar adsorption state was observed [13]. It was proposed that the decomposition of TMG mostly follows an intramolecular process on Si(100). Upon heating, one of the methyl groups in TMG reacts with another methyl groups and produces methane and Ga–CH₂ fragment.

* Author to whom correspondence should be addressed. E-mail: ysma@ustc.edu.cn

The remaining methyl groups react with CH₂ fragment and release methane upon further annealing at higher temperature. At even higher temperature, CH species decompose to produce carbon and H₂ [13]. Only few investigations have dealt with the adsorption and decomposition of TMG on metal substrate [9, 11]. Zhou, Liu, and coworkers have studied the interaction of TMG with Ni(111) and Pt(111) previously by temperature programmed desorption (TPD), static secondary ion mass spectrometry, high-resolution electron energy loss spectroscopy [9, 11]. It has been found that the adsorption and reaction on more active metal surface is largely different from that on semiconductor substrates. On Ni(111), TMG adsorbs dissociatively at a low temperature of 100 K and low exposure, leaving Ga, CH₃, and Ga(CH₃)₂ (DMG) on the surface [9]. At higher exposure, TMG molecular adsorption is observed. Upon heating, TMG and DMG undergo stepwise dissociation of Ga–C bonds and the formed CH₃ fragment may undergo dehydrogenation below 150 K or hydrogenation to CH₄ at higher temperature (250 K). The final products after the complete decomposition at higher temperature are Ga and C [9]. On Pt(111), TMG also adsorbs dissociatively even at a low temperature of 120 K via the cleavage of Ga–C bond, producing CH₃(a) and Ga(CH₃)₂ adsorbed on Pt substrate [11]. After heating to higher temperature, the decomposition of TMG also proceeds through stepwise dissociation of Ga–C bonds while the formed methyl species undergo dehydrogenation or hydrogenation with CH₄ and H₂ as the only desorption products.

In the present study, the interaction of TMG with Pd(111) has been studied using TPD and X-ray photoelectron spectroscopy (XPS). It is found that TMG adsorb dissociatively on Pd(111) even at 140 K. Upon heating, TMG undergoes a stepwise dissociation with CH₄ and H₂ as the desorption products. The molecular desorption of Ga-containing species is also identified. Furthermore, the effect of precovered H and oxygen on the adsorption and decomposition behavior has also been investigated. The results are discussed in comparison with those obtained on clean Pd(111).

II. EXPERIMENTS

All experiments were performed in a home made stainless-steel ultrahigh vacuum (UHV) chamber with a base pressure of 2×10^{-10} mbar. The UHV chamber was equipped with facilities for XPS, low energy electron diffraction (LEED), and differential-pumped TPD measurements. A Pd(111) single crystal (purchased from MaTeck) was mounted on the sample holder by two Ta wires spot-welded to the back side of the sample. The sample was cooled by liquid nitrogen and heated resistively. Temperatures could be controlled between 135 and 1200 K and were measured by a chromel-alumel thermocouple spot-welded to the backside of

the sample. Prior to the experiment, Pd(111) was cleaned by repeated cycles of Ar ion sputtering, oxidation (6.65×10^{-8} mbar O₂, $T=900$ K), and annealed until LEED gave a sharp diffraction pattern and no contaminants could be detected by XPS.

TMG (>99.999%, Jiangsu Nata Opto-Electronic Material Co. Ltd.) was introduced with N₂ as carrier gas by a line of sight stainless steel doser (diameter of 8 mm), which is positioned ~ 1 cm in front of the sample. The hydrogen (>99.9%, Nanjing ShangYuan Industry Factory) and oxygen (>99.9%, Nanjing ShangYuan Industry Factory) were dosed by backfilling. The purity of all gases and reactants was checked by quadrupole mass spectrometer (QMS, Pfeiffer Vacuum QME 220) prior to experiments. All exposures were reported in Langmuir ($1 \text{ L} = 1.33 \times 10^{-8}$ mbar·s) without correction of ion gauge sensitivity. Specially, the exposure of TMG was reported here without considering the enhancement factor of doser.

During the TPD experiments, the sample was positioned ~ 1 mm away from the collecting tube of a differentially-pumped QMS and heated to 600 K with a heating rate of 3.0 K/s. XPS spectra were recorded by a hemispherical energy analyzer (PHBIOS 100 MCD, SPECS GmbH) with a pass energy of 20 eV using Al K α radiation ($h\nu=1486.6$ eV). By using the XPS Peak 4.1 software, the C 1s XPS spectra was curve-fitted by a mixture of Gaussian and Lorentzian function after subtracting of a Shirley background. All binding energies are referenced to the Fermi level with the Pd 3d_{5/2} peak of clean Pd substrate at 335.0 eV. For the annealing experiments, the substrate was heated to desired temperature and was held for 30 s.

III. RESULTS AND DISCUSSION

A. Adsorption and decomposition of Ga(CH₃)₃ on clean Pd(111)

Figure 1 displays the CH₄ ($m/z=16$) and H₂ ($m/z=2$) TPD spectra after exposure of various amounts of Ga(CH₃)₃ to clean Pd(111) at 140 K. In TPD spectra, CH₄ ($m/z=16$) and H₂ ($m/z=2$) are the only detected desorption products for all the studied exposures. The 15 amu signal is always detected with very similar peak shape, intensity and position with that of 16 amu, suggesting the desorption signal is due to CH₄, not CH₃⁺ radical. The molecular desorption of Ga(CH₃)_{*x*} ($x=1, 2, \text{ or } 3$) as well as other hydrocarbon molecules (such as C₂H₄, C₂H₆ *etc.*) was not observed under the present experimental condition. At exposure of 0.05 L, two CH₄ desorption peaks were observed: a broad one at 196 K with a low-temperature tail at 160 K and a narrow peak at 290 K, respectively. Since the desorption temperature for CH₄ adsorption on Pd(111) alone is below 100 K [15], the observed CH₄ desorption features should be reaction-

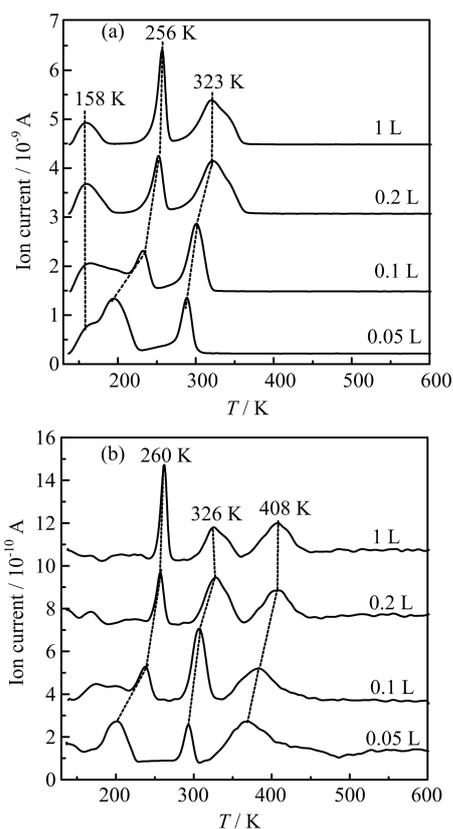


FIG. 1 (a) CH₄ ($m/z=16$) and (b) H₂ ($m/z=2$) TPD spectra following the indicated exposures of TMG on Pd(111) at 140 K.

rate limited. The following XPS results suggest that these three peaks should come from the decomposition/reaction of TMG and its dissociation intermediates such as dimethylgallium (Ga(CH₃)₂, DMG) and monomethylgallium (GaCH₃(a), MMG) and will be discussed later. Simultaneously, four H₂ desorption peaks (2 amu) are detected at 160, 200, 294, and 366 K in the TPD spectra, respectively. The desorption temperatures of the former three features are similar with those of CH₄ desorption signals in the obtained TPD spectra, implying the same origin for both desorption products. The additional broad H₂ desorption signal around 366 K is possibly due to the associative desorption of H(a) on Pd(111) [16]. With increasing TMG exposure, the desorption temperature of CH₄ peak at 160 K is kept almost constant while the CH₄ desorption peaks at 196 and 290 K shift to higher temperature gradually. Upon exposure of 0.2 L, the desorption of three CH₄ peaks appears at 160, 256, and 320 K, respectively. In the case of 2 amu, except the signals accompanying with the 16 amu signal, an additional H₂ desorption was also observed at 407 K at TMG exposure of 0.2 L. This H₂ desorption feature exhibits a higher desorption temperature than the recombinative desorption, which is assigned to the dehydrogenation of CH_x species [17, 18].

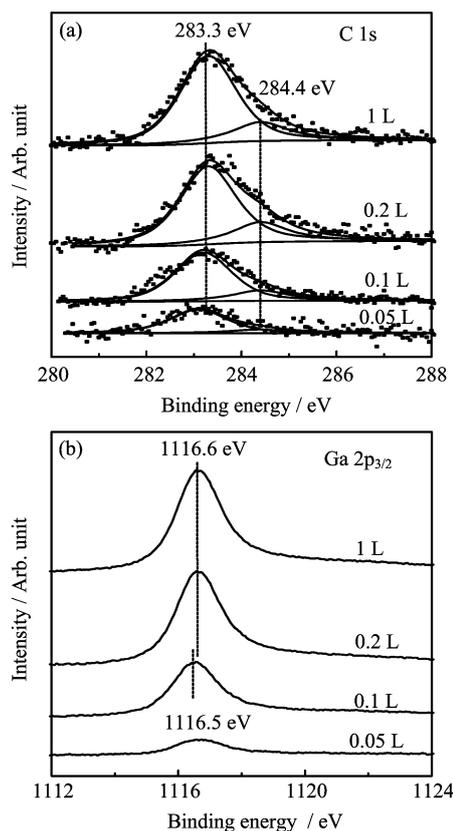


FIG. 2 (a) C 1s and (b) Ga 2p_{3/2} XPS spectra obtained after various TMG exposures on Pd(111) at 140 K.

The adsorption and decomposition of TMG on Pd(111) was monitored by XPS measurements. Figure 2 displays C 1s and Ga 2p_{3/2} XPS spectra after Pd(111) was exposed to various amounts of TMG at 140 K. At low TMG exposure of 0.05 L, the Ga 2p_{3/2} spectrum exhibits a small band at 1116.5 eV. Increasing the TMG exposure causes a small positive shift of the binding energy of Ga 2p_{3/2} by 0.1 eV as well as an enhancement of the intensity. On Si(100), the binding energy of Ga 2p_{3/2} is 1117.2 eV for molecular TMG and 1116.9 eV for chemisorbed Ga metal [13]. Although the binding energy of Ga 2p_{3/2} is not a sensitive parameter to differentiate TMG and its dissociation products (Ga(CH₃)_x, $x=1, 2$, or 3), the observed positive shift of the binding energy of Ga 2p_{3/2} with increasing exposure as well as the following annealing experiments may imply that TMG adsorbs dissociatively at low exposure leaving some Ga(CH₃)_x ($x=1$ or 2) species on the surface. At the same time, the C 1s spectrum is fitted by two peaks located at 283.3 and 284.4 eV at exposure of 0.05 L. The former feature is ascribed to the adsorbed TMG and its dissociation intermediate such as DMG/MMG, all of which have been reported to exhibit a similar binding energy (283.5 eV) after TMG adsorption on Si(100) [13, 19]. The latter peak at 284.4 eV is usually a characteristic of CH_x(a) species on Pd sub-

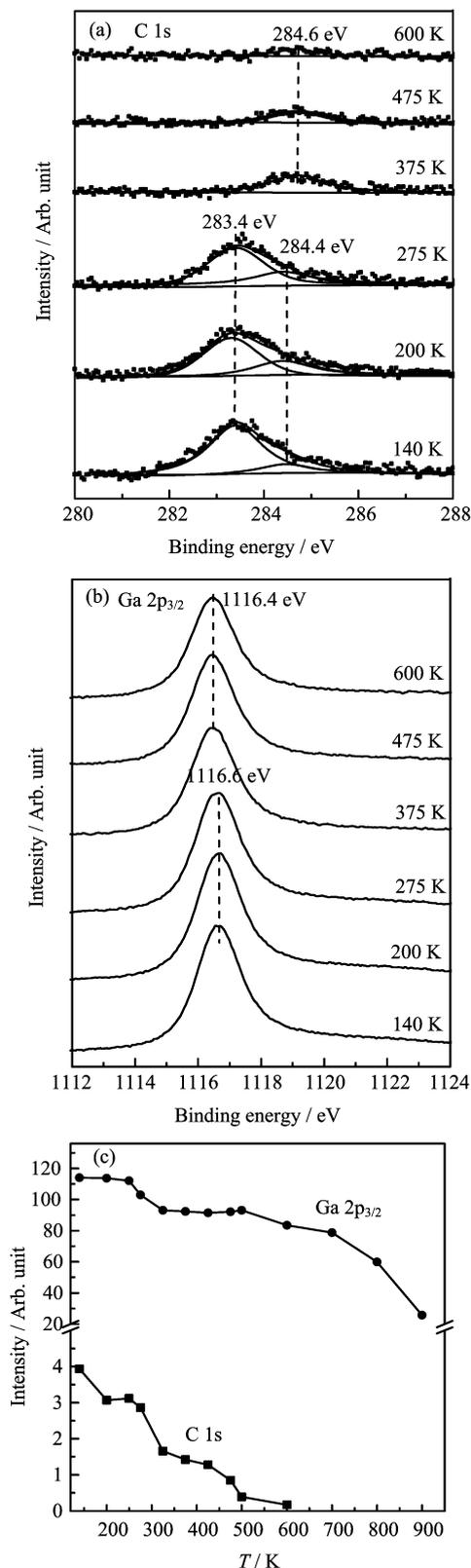


FIG. 3 (a) C 1s Ga and (b) 2p_{3/2} XPS spectra obtained after Pd(111) was exposed to 0.2 L TMG at 140 K and followed by subsequent annealing to the indicated temperatures. (c) The corresponding integrated peak areas of Ga 2p_{3/2} and C 1s components as a function of annealing temperature.

strate [17, 20, 21]. So it may also suggest that TMG partly adsorbs dissociatively at 140 K, leaving CH_x(a) and Ga(CH₃)₂ (or Ga(CH₃)) species on the surface. Considering the atomic sensitivity factor [22], the ratio of C to Ga is ~ 0.43 for 0.2 L exposure at 140 K compared to the value of 3 for molecular TMG. It also suggests that TMG adsorbs dissociatively on Pd(111) releasing CH₄ into gas phase. This assumption is further supported by the observation that CH₄ desorption starts immediately at the beginning of TDS measurement. The dissociative adsorption of TMG was also observed on Ni(111) and Pt(111) [9, 11]. On both metal surface, TMG partly decomposes into DMG and CH₃ after adsorption at 100–120 K, in contrast to molecular adsorption on Si substrate [12–14]. So, it indicates that metal surfaces are more reactive towards TMG dissociation compared to semiconductor substrates. With increasing TMG exposure, the C 1s peak at 283.3 eV is largely enhanced, suggesting an increase of Ga(CH₃)_x ($x=1, 2, \text{ or } 3$) coverage.

Figure 3 shows the C 1s and Ga 2p_{3/2} XPS spectra and the corresponding integrated intensity acquired after Pd(111) was exposed to 0.2 L TMG at 140 K followed by annealing at various temperatures. As shown above, exposure of 0.2 L TMG gives rise to two features in the C 1s region: one main component at 283.4 eV and another one at 284.4 eV. These features are ascribed to the surface species such as Ga(CH₃)_x ($x=1-3$) and CH_x(a) formed during the dissociative adsorption of TMG. Annealing to 200 K causes a slight decrease in the intensity of the C 1s feature at 283.4 eV, in consistent with CH₄ desorption at 160 K. After annealing at 275 K, the feature at 283.4 eV decreases gradually in intensity while the component at 284.4 eV is kept almost constant. It clearly indicates that the former feature is responsible for the CH₄ desorption peak at ~ 256 K. Upon annealing at 375 K, the C 1s component at 283.4 eV disappears completely, corresponding to the CH₄ and H₂ desorption observed at ~ 320 K (Fig.1). Further heating to 475 K induces a single C 1s peak at 284.6 eV, which is reasonably ascribed to carbonaceous C(a) left by the dehydrogenation of CH_x(a) [23]. It agrees well with the H₂ desorption peak at 405 K observed in TPD spectra (Fig.1). Moreover, the intensity of C 1s decreases gradually above 375 K and almost no C 1s signal is detected at 600 K. It was explained by C diffusion into the bulk of Pd substrate since only H₂ desorption was observed above 350 K in the TPD spectra [17, 24, 25]. In the case of Ga 2p_{3/2}, the binding energy is kept constant at 1116.6 eV up to 275 K. Above 325 K, it shows a negative shift by 0.1 eV. In previous literatures, a similar negative shift has been reported in Ga 2p_{3/2} spectra when annealing TMG-adsorbed Si(100), which was explained by decomposition of Ga(CH₃)_x to metal Ga [13]. So it may indicate that the Ga–C bond was broken completely above 375 K leaving adsorbed Ga(a) on the surface. In addition, a distinct attenuation of Ga 2p_{3/2} peak is

observed in the temperature of 275–325 K. Since the desorption temperature of metallic Ga was reported to be above 800 K [11, 13], it clearly suggests that some Ga-containing molecules (probably Ga(CH₃)_x) desorb from the surface along with reaction-limited CH₄ desorption although the TPD results did not detect any Ga(CH₃)_x desorption. The absence of Ga(CH₃)_x signal is probably due to its facile decomposition in the ionizer of mass spectrometer and/or the desorption signal is beyond the detection limit of QMS. The desorption of Ga-containing molecules on Pd(111) is a little surprising since there is no evidence for such desorption except for multilayer TMG on other metal surfaces such as Ni(111) and Pt(111) [9, 11]. However, the molecular desorption of MMG was observed above 473 K on Si(111) [14]. Above 325 K, the intensity of Ga 2p_{3/2} remains almost constant up to 500 K. At higher temperature, Ga starts to diffuse into Pd substrate and causes the formation of Pd–Ga alloy [26].

On the basis of the above TDS and XPS results, the adsorption and decomposition of TMG on Pd(111) was proposed as the following: TMG adsorbs dissociatively upon exposure at 140 K and the surface is covered by a mixed Ga(CH₃)_x and CH_x(a) layer. It was reported that CH₃(a) is very active and easily hydrogenates/dehydrogenates into CH₃(g) below 200 K [15, 27]. Therefore, the observed three reaction-limited CH₄ desorption peaks accompanied by H₂ desorption peaks in the TDS spectra are ascribed to the hydrogenation of CH₃(a) formed by the stepwise dissociation of TMG. That is, the rate of CH₄ desorption is determined by the cleavage of Ga–C bond in adsorbed Ga(CH₃)_x species and the hydrogenation/dehydrogenation of CH₃(a) occurs promptly after it is formed. At 160 K, TMG dissociates into DMG and CH₃(a) and the latter species may hydrogenate/dehydrogenate after its formation releasing CH₄ and H₂ into gas phase [27]. Around 250 K, DMG further decomposes into MMG and the resultant CH₃(a) again formed CH₄(g) and H₂ leaving CH_x(a) species on the surface. In the temperature range of 250–320 K, the decomposition of MMG is accompanied by the molecular desorption of MMG, as supported by the decrease of the intensity of Ga 2p_{3/2} signal in XPS spectra (Fig.3(c)). It should be noted that the formation of CH₄(g) via the intermolecular/intramolecular reaction of Ga(CH₃)_x cannot be excluded on the basis of the above results. At a temperature of 375 K, only Ga(a) and CH_x(a) are left on the surface. The CH_x(a) species dehydrogenate and produce carbon deposits and H₂(g) around 400 K. After complete decomposition of TMG, carbon deposits and metallic Ga are left on the surface, both of which start to diffuse into the bulk of Pd substrate at higher temperature.

B. The effect of pre-covered H

The effect of pre-covered H for TMG adsorption and decomposition was studied by using TPD and XPS

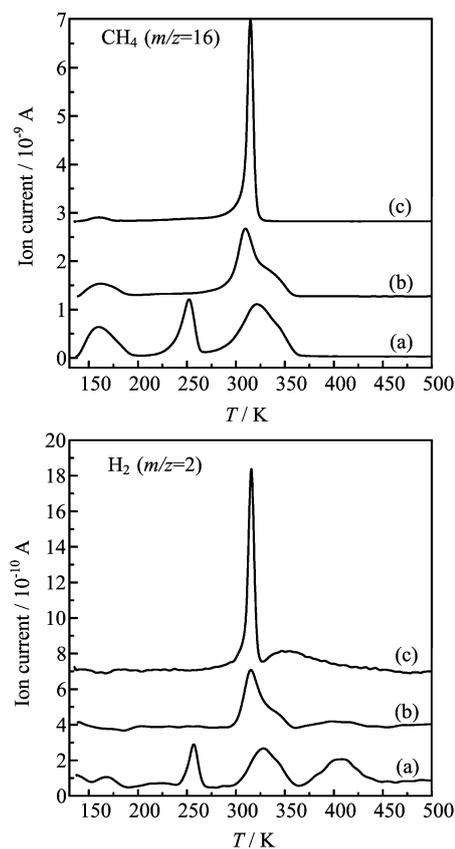


FIG. 4 CH₄(*m/z*=16) and H₂ (*m/z*=2) TPD spectra for (a) clean Pd(111), (b) Pd(111) was exposed to saturated H₂ at 140 K, and (c) Pd(111) was exposed to saturated H₂ at 200 K followed by 0.2 L exposure of TMG at 140 K.

measurement. Previous reports show that the state of adsorbed H species on Pd samples depends on the substrate temperature during H₂ exposure [28, 29]. Increasing the substrate temperature usually induces H₂ diffusion into the bulk of the Pd sample [28, 29]. In the present study, two types of pre-covered H species were prepared by changing the substrate temperature before TMG adsorption on Pd(111) and then the results are compared with those on clean Pd(111). Figure 4 shows the CH₄ and H₂ TPD spectra after exposure of 0.2 L TMG on H-precovered Pd(111). When saturated H₂ was pre-dosed at 140 K, CH₄ mostly desorbs at 315 K and a shoulder peak was observed at 330 K. The maximum of the main desorption peak is slightly lower than that of TMG adsorption on clean Pd(111) (322 K). Furthermore, the CH₄ desorption signal at 160 K is largely attenuated and the peak at 250 K completely disappears. Similarly, a single H₂ desorption peak was observed at 315 K accompanied by a shoulder peak at 330 K. Furthermore, the H₂ desorption peak at 407 K, which results from CH_x dehydrogenation, is almost negligible. When H₂ was pre-exposed at 200 K, both CH₄ and H₂ desorption exhibit a single sharp peak at 315 K. Additionally, a small H₂ signal was also observed at

340 K, assigned to recombinative desorption of H(a).

XPS measurements was also used to examine the surface intermediate and composition during TMG decomposition on H-precovered Pd(111). Figure 5 (a) and (b) show C 1s and Ga 2p_{3/2} spectra obtained during the annealing process of Pd(111) which was firstly pre-dosed to H₂ at 140 K and then exposed to 0.2 L TMG at the same temperature. Correspondingly, the changes of the intensity are displayed as a function of annealing temperature in Fig.5(c). When 0.2 L TMG was exposed to H-precovered Pd(111), the C 1s XPS spectra exhibit a broad band with the maximum at 283.4 eV together with a high-energy tail. Fitting the C 1s spectra gives rise to two components with the binding energy at 283.4 and 284.4 eV. Again, the former feature corresponds to Ga(CH₃)_x(a) while the latter results from CH_x(a) produced by the decomposition of TMG. In the Ga 2p_{3/2} region, a single peak was observed at 1116.6 eV, corresponding to adsorbed Ga(CH₃)_x species. Annealing at the temperature up to 250 K induces no significant changes of both C 1s and Ga 2p_{3/2} features, in agreement with the observation that almost no desorption was detected in the TPD measurement (Fig.4). In the annealing temperature range of 275–325 K, the C 1s peak at 283.4 eV largely decreases in intensity. At the same time, the Ga 2p_{3/2} peak experiences a negative shift to 1116.5 eV as well as a decrease in intensity. The above observations indicate that the Ga(CH₃)_x(a) species undergoes two competitive reaction channels between 275–325 K on H-precovered Pd(111): the desorption of Ga(CH₃)_x species versus the decomposition of Ga(CH₃)_x(a) with CH₄ and H₂ as the dissociation products. Above 375 K, only carbon deposits (C 1s peak at 284.6 eV) and metallic Ga(a)(Ga 2p_{3/2} peak at 1116.5 eV) are left on the surface, both of which start to diffuse into the bulk of Pd substrate at higher temperature.

As discussed above, the rate-limiting step of CH₄ desorption is the formation of CH₃(a) produced by the dissociation of Ga(CH₃)_x species. The presence of precovered-H clearly suppresses the CH₄ desorption peaks at ~160 and 250 K, which are assigned to the hydrogenation of CH₃(a) formed by the dissociation of TMG and DMG, respectively. And the situation becomes more significantly when the surface is precovered by subsurface H(a) (Fig.4). So it may suggest that the TMG mostly dissociates into MMG upon adsorption at 140 K in the presence of H(a) since H(a) can react easily with CH₃(a) and promote the cleavage of Ga–C bond. As a result, the reaction channel of DMG is largely suppressed and the desorption and dissociation of MMG becomes dominant in subsequent annealing process.

C. TMG decomposition on O-precovered Pd(111)

TMG is not an appropriate Ga source for film deposition since unwanted residual carbon is left during TMG

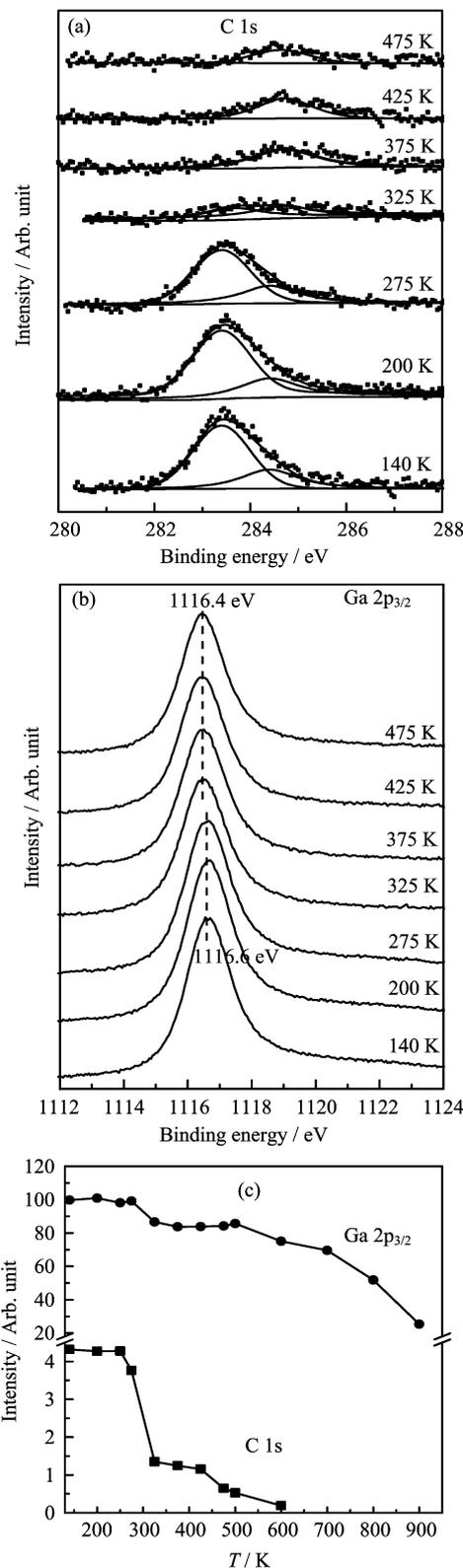


FIG. 5 (a) C 1s and (b) Ga 2p_{3/2} XPS spectra obtained after Pd(111) was first saturated by H₂ at 140 K, and then exposure of 0.2 L TMG at 140 K and subsequent annealing to the indicated temperatures. (c) The corresponding integrated peak areas of Ga 2p_{3/2} and C 1s components as a function of annealing temperature.

deposition [13]. On the other hand, one facile way to deposit Ga₂O₃ film by atomic layer deposition is to provide various oxygen sources such as O₂ and O₃ during TMG interaction with the substrate, as demonstrated in Ref.[4]. Therefore, in the present study, the effect of pre-covered oxygen on the adsorption and decomposition behavior of TMG was further examined.

Before TMG exposure, oxygen was exposed to Pd(111) at two different substrate temperatures of 140 and 300 K. It has been found that oxygen adsorbs dissociatively on Pd(111) above 200 K [30]. Therefore, O₂ exposure at 140 K corresponds to molecular oxygen species while exposure at room temperature produces atomic oxygen. Figure 6 displays the CH₄ and H₂ TPD results obtained after Pd(111) were pre-covered by saturated O₂(a) and O(a) followed by exposure of 0.2 L TMG at 140 K. In the presence of adsorbed O₂(a), the CH₄ peak at 258 K gains in intensity and the others attenuate while the desorption temperatures of all the CH₄ desorption peaks remain almost unchanged with respect to the case of clean Pd(111). It suggests that the reaction channel at 250 K is preferred while the reaction channels for H₂ and CH₄ formation at 160 and 330 K are suppressed by preadsorbed O₂. The situation becomes more significant for atomic O-precovered Pd(111). For both CH₄ and H₂ desorption, the desorption peak at 258 K is largely enhanced while that at 320 K disappears completely. Meanwhile, the H₂ desorption peak at 409 K due to CH_x dehydrogenation remains almost constant. It should be mentioned that no O₂ desorption was observed in the studied temperature range (140–900 K). On clean Pd(111), it was reported that recombinative oxygen desorption occurs at 800 K [30]. A small peak of H₂O was detected at ~500 K, which may be ascribed to OH disproportionation. Such H₂O desorption is consistent with an observation that Auger KLL peak of oxygen decreases in intensity in the temperature of 475–500 K (not shown).

The TMG decomposition behavior on O-precovered Pd(111) was monitored by XPS measurements. Figure 7 shows C 1s, Ga 2p_{3/2} XPS spectra and the corresponding integrated intensity as a function of annealing temperature, which was recorded after Pd(111) was firstly exposed to saturated O₂ at 300 K and then to 0.2 L TMG at 140 K. The saturation coverage of O was reported to be 0.25 ML on Pd(111) at room temperature [30]. The O 1s peak is not shown here since it is overlapped with Pd 3p_{3/2} peaks and cannot provide the information of the chemical state of adsorbed O. Upon exposure of O-covered Pd(111) to TMG at 140 K, fitting the C 1s region gives rise to three C 1s features with binding energy at 282.6, 283.3, and 284.4 eV, respectively. The C 1s peak at 282.6 eV is predominant after 0.2 L TMG adsorption on O-precovered Pd(111), very different from that observed on clean Pd(111) in which the main C 1s component is located at 283.4 eV (Fig.2(b)). As shown before, the feature at 283.3 and 284.4 eV can be attributed to Ga(CH₃)_x(a) and

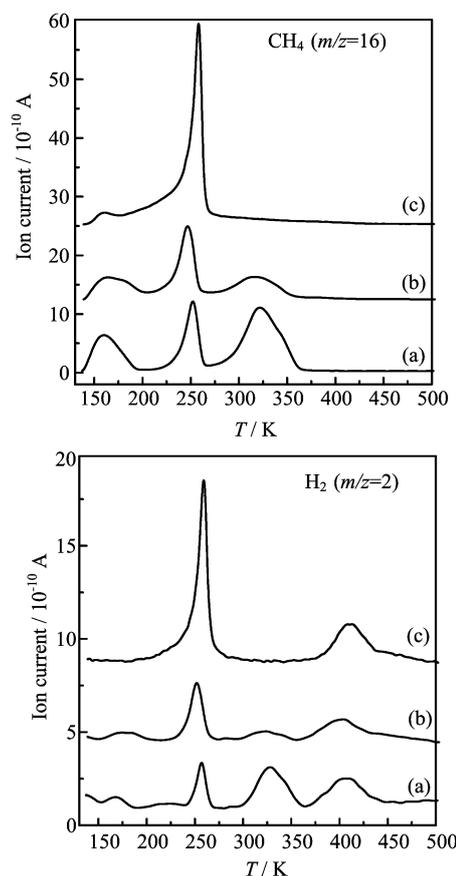


FIG. 6 CH₄ ($m/z=16$) and H₂ ($m/z=2$) TPD spectra for (a) clean Pd(111), (b) Pd(111) was exposed to saturated O₂ at 140 K and (c) Pd(111) was exposed to saturated O₂ at 300 K followed by 0.2 L exposure of TMG at 140 K.

CH_x(a) adsorbed on bare Pd substrate since O(a) coverage is only 0.25 ML and some Pd sites are still available for adsorption in the present study. The formation of oxygenated carbon species such as adsorbed methoxy (OCH₃(a)) and dioxymethylene (CH₂O₂(a)) can be ruled out as indicated by the absence of C 1s feature above 286 eV [20, 31]. At the same time, Ga 2p_{3/2} shows a single peak at 1116.6 eV similar to the case on clean Pd(111), supporting Ga(CH₃)_x species, not metallic Ga, to be the predominant Ga species. When increasing the surface temperature up to 225 K, the C 1s feature at 282.6 eV attenuates largely while the intensities of those at 283.3 and 284.4 eV are kept almost constant. Simultaneously, the Ga 2p_{3/2} peak shifts to a higher binding energy by 0.4 eV, suggesting Ga(a) is “oxidized” by preadsorbed oxygen. In comparison with the TDS results, the evolution of C 1s region clearly indicates that the surface species with a C 1s feature at 282.6 eV is responsible for the CH₄ and H₂ desorption at 258 K. After heating to 275 K, the C 1s feature at 282.6 eV disappears completely and two C 1s features are resolved to be located at 283.3 eV (Ga(CH₃)_x(a) species) and 284.4 eV (CH_x(a) species),

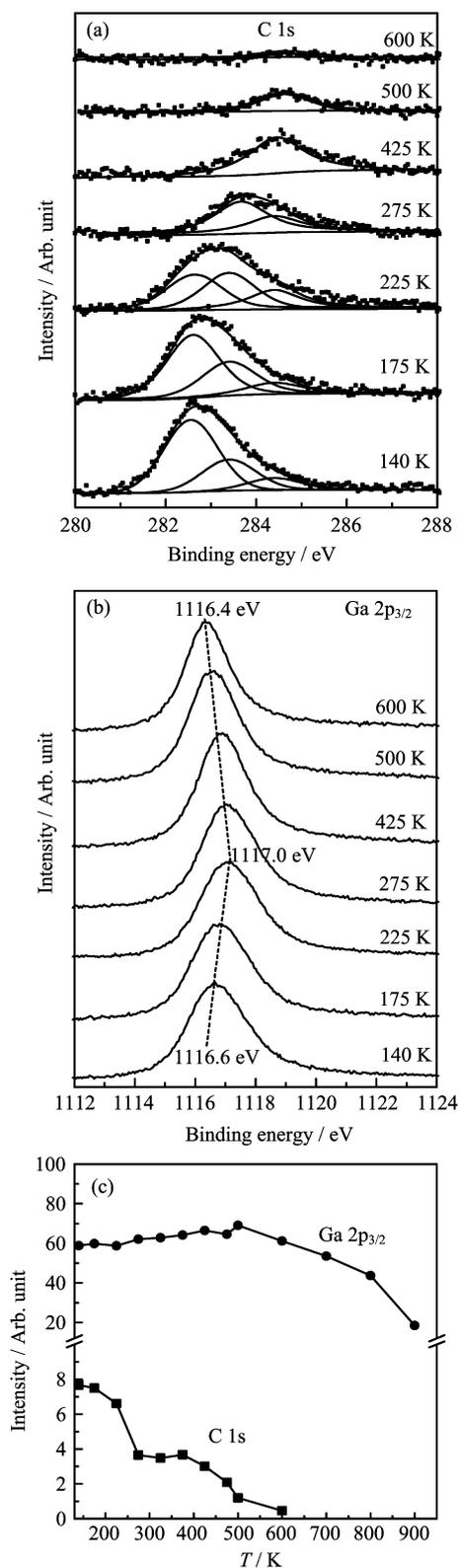


FIG. 7 (a) C 1s and (b) Ga 2p_{3/2} XPS spectra obtained after Pd(111) was first saturated by O₂ at 300 K, and then exposure of 0.2 L TMG at 140 K and subsequent annealing to the indicated temperatures. (c) The corresponding integrated peak areas of Ga 2p_{3/2} and C 1s components as a function of annealing temperature.

respectively. Upon heating to 425 K, the C 1s feature exhibits a broad peak at 284.6 eV, which was reasonably attributed to C(a) left by the dehydrogenation of CH_x species. It agrees well with the H₂ desorption peak at 409 K. At higher temperature, C(a) starts to diffuse into the bulk and cause an attenuation of C 1s peak. In the case of Ga 2p_{3/2}, the intensity remains almost constant up to 500 K, suggesting that the desorption of any Ga-containing species is negligible below that temperature. Moreover, the binding energy of Ga 2p_{3/2} shows a negative shift in the temperature range of 425–500 K. Above that, Ga starts to diffuse into Pd substrate accompanied with the formation of Pd–Ga alloy, which cause a decrease in the intensity of Ga 2p_{3/2} feature.

The origin of the C 1s feature at 282.6 eV is still not clear. Usually, carbide species shows a C 1s peak at 282.5 eV [22]. In the case of TMG adsorption on Si(100), the C 1s feature at 282.5 eV was assigned to chemisorbed carbon [12, 13]. However, the assignment to carbide or chemisorbed carbon is not likely in the present study since TDS and XPS results indicate that this C 1s feature is related to simultaneous desorption of CH₄ and H₂ at 258 K. Furthermore, the dissociation temperature of this species is very close to that of Ga(CH₃)₂ on bare Pd(111), as discussed above. Here, we tentatively assigned the C 1s peak at 282.6 eV to Pd–O–Ga(CH₃)₂ species produced by dissociative adsorption of Ga(CH₃)₃ on O-covered Pd(111). A similar structure was reported to be formed (Al–O–Al(CH₃)₂) in the reaction between trimethylaluminum and H₂O during the controlled deposition of Al₂O₃ film [32].

IV. CONCLUSION

TMG adsorbs dissociatively on clean Pd(111) at 140 K, leaving a mixture of Ga(CH₃)_x and CH_x(a) species on the surface. Upon annealing, the dissociation of TMG may undergo a stepwise cleavage of Ga–C bond while CH₃(a) hydrogenates/dehydrogenates immediately after its formation releasing CH₄(g) and H₂(g), which are observed at about 160, 260, and 320 K, respectively. XPS results strongly suggest that the dissociation of MMG is accompanied by the molecular desorption of Ga(CH₃)_x species (probably GaCH₃) at 320 K. Saturating the surface with H(a) significantly suppresses the dissociation channels at 160 and 260 K while simultaneous desorption of CH₄ and H₂ are mostly observed at 320 K. It is assigned to the dissociation products after TMG adsorption on H(a)-precovered Pd(111). Upon exposure of TMG on O(a)-precovered Pd(111), CH₄ and H₂ are the only desorption products in the subsequent heating. A Pd–O–Ga(CH₃)₂ structure is proposed to be the decomposition intermediate. Furthermore, there is no evidence for the molecular desorption of Ga-containing species on O(a)-precovered Pd(111) in contrast to the case of clean and

H(a)-precovered Pd(111).

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