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Pyrolytic and Photolytic Dissociation of Trimethylgallium on Si, Au, and Al Substrates

S. SHOGEN, Y. MATSUMI, M. KAWASAKI and I. TOYOSHIMA*

Research Institute of Applied Electricity and
Research Center for Catalysis*, Hokkaido University
Sapporo 060, Japan

Pyrolytic and photolytic dissociation of trimethylgallium on Si, Au and Al substrates was studied by X-ray and UV photoelectron spectroscopy technique. On an Si(111) substrate, gallium metal and CH_n radicals are deposited by pyrolytic dissociation up to 670 K. On a polycrystalline Au substrate, gallium metal was observed while C1s signal disappeared at 470 K. Photodissociation of monolayered $Ga(CH_3)_2$ at 266 nm gives XPS spectra for CH_n radicals and Ga metal on the Si wafer while at 355 nm no decomposition was observed.

1. Introduction

Surface reactions involving metal alkyls are of interest because of their importance in the deposition of thin epitaxial films for the fabrication of microelectronic devices. Consequently, there have been considerable interests in using external energy sources such as photons to stimulate the growth of metals on surfaces. Several studies of laser-enhanced metal-organic chemical vapor deposition have been reported. Ehrlich and Osgood [1] demonstrated laser-assisted CVD of organometallic compounds. More recently, McCaulley et al [2] reported XPS studies of laser-stimulated decomposition of TMGa adsorbed on GaAs substrates. Nishizawa et al [3] and Doi et al [4] reported MOCVD by laser irradiation. These processes involve the interaction of a metal alkyl with a substrate. Surface chemistry determines the nature of the surface and also provides the adspecies with which incident photons must interact. Despite their importance, little direct information is available on these surface reactions.

2. Experimental

An apparatus (VG-ESCA Mark II) consists of an analysis chamber and a sample preparation chamber for substrate cleaning and dosing with TMGa. An Si(111) single crystal wafer (Osaka Titanium Inc.), poly-crystalline Au and Al plates (99.999%) were held on a sample holder attached with resistive heating and liq. N_2 cooling. The substrates were cleaned in the preparation chamber by Ar^+ bombardment, resistive heating and irradiation by an IR lamp. After cleaning, no impurities were observed by XPS. The vacuum system has a base pressure in $1x10^{-10}$ Torr range. The substrate cooled to 80 K was exposed with TMGa gas at a pressure of $1x10^{-8}$ Torr for 20 min so that multilayers was formed on the cooled substrate. After this procedure, the substrate was transferred to the adjacent chamber for analysis using X-ray (XPS) photoelectron spectroscopy. For pyrolysis experiment, the substrate holder is resistively heated up to 670 K. Typically at 170 K, a monolayer of TMGa was formed on a substrate. The analyzer was calibrated using

the Si2p photoelectron peak at 99.15 eV. The binding energy of C1s was also observed in pyrolysis of azomethane. The CH_3 radicals on Si and Au have values of 285.8 and 285.2 eV, respectively. Ga3d signals of metallic Ga appeared at 18.5 eV. Atomic sensitivity factor [5] is a function of TMGa layers and also an angle of analyzer. The factors are 0.25 for C1s, 0.38 for N1s, 0.31 for Ga3d, 5.8 for $Ga2p_{3/2}$, 0.17 for Si2p, 1.9 for $Au4f_{7/2}$, 0.11 for Al2p.

The third- and fourth-harmonics of a YAG laser(SP DCR-11) delivered pulse energies of 48 and 24 mJ, respectively, at a repetition rate of 10 Hz. The unfocused laser beam was imaged vertically onto the substrate. A He I line at 58.4 nm was also used as a photolysis lamp. TMGa gas (electronics grade) was kindly supplied from Sumitomo Chemicals and used without further purification.

3. Results and Discussion

a) Pyrolysis of TMGa on Si

TMGa on the Si substrate was heated up to 670 K. The change of the XPS spectra is shown in Fig. 1. At 80 K, physisorbed multilayers are formed since the Ga3d and C1s peaks shift toward higher binding energies, probably caused by the charge-up of the solid molecules. Upon increasing the substrate temperature to 120 K, the signal intensities and the values of the binding energy start to decrease. Temperature increase causes desorption and decomposition of TMGa from the substrate as shown in Fig. 2. The carbon concentration decreased by a factor of five when the temperature was changed from 80 K to 170 K. Above this temperature, the carbon intensity changes slightly with increasing substrate temperatures. This result suggests that the substrate was covered with a monolayer of $Ga(CH_3)_2$ at this temperature.

When the substrate is heated from 170 K to 670 K, the binding energy of Ga3d is shifted from 19.5 eV to 18.2 eV. The value of 18.5 eV corresponds to that of Ga metal. This result suggests that $Ga(CH_3)_3$ decomposes to Ga metal on the Si substrate. Since Ga is a trivalent metal, its three electrons are involved in the covalent bonds which are formed with the three neighboring Si surface atoms.[7] The charge transfer leaves an electric dipole normal to the surface with the positive charge on the outside, thus decreasing the binding energy of Ga compared with that of TMGa.

By additional heating with an IR lamp, the signal of Ga3d disappeared because of vaporization of Ga metal. Temperature increase shifts the C1s signal toward lower binding energies and enlarges the FWHM of the signals centered at 284.5 eV. Steinbach et al [8] reported that CH_3, CH_2, CH, and C species have binding energies higher than C by 2.7, 1.8, and 0.7 eV respectively. The carbon species formed on the Si surface are mainly CH_2. Lee et al [9] reported in HREELS measurement that the intermediate species is CH_2 on a Si(100) substrate in pyrolysis of TMGa.

The ratios of carbon to gallium are plotted as a function of substrate temperature in Fig. 2. At 80 K, the ratio is three but starts decreasing at > 170 K. At > 290 K, the ratio is close to two. This fact suggests that $Ga(CH_3)_2$ is formed on the substrate and is in agreement with the HREELS study of Lee et al [9].

b) Pyrolysis of TMGa on Au

After deposition of TMGa on the Au substrate at 80 K, this substrate was heated up to 670 K. The XPS spectra are given in Fig. 3. Temperature dependence of Ga3d and C1s signal intensities is shown in Fig. 4. The peak of Ga3d shifted toward lower binding

energies at higher temperatures. Metallic Ga is formed from TMGa on Au. The behavior of the Ga3d signals is the same as that observed on the Si substrate. However, the behavior of the C1s signal is different from that observed on the Si. The C1s signal disappeared at 570 K, suggesting that CH_3 radicals desorb easily from the Au substrate.

c) Pyrolysis of TMGa on Al

TMGa was deposited on an Al substrate at 80 K. The substrate was heated up to 170 K as shown in Fig. 5. The fact that Ga3d peak was shifted to 18.5 eV means that Ga metal is already formed at 170 K. Dissociation of TMGa to atomic Ga and CH_n(n=1-2) occurs even at 170 K on the Al substrate. Above this temperature, the substrate surface is contaminated with CO_x, an impurity gas, in the chamber. No reliable data were not obtained for C1s signals at T > 170 K.

d) Photolysis of TMGa on Si

When the substrate temperature was increased from 80 K to 290 K, a monolayer of $Ga(CH_3)_2$ was formed. Laser irradiation of this monolayer at 266 nm gives the XPS spectra of Fig. 6. The C1s peak shifts toward higher binding energies. This result suggests that methyl radicals are generated on the Si surface from Ga-C bond scission by photoexcitation. Ga3d signals shift slightly toward lower binding energies, suggesting little formation of metallic Ga on the Si surface. By 355 nm irradiation, no signal change was observed. Since photoabsorption of TMGa on synthetic silica starts at 250 nm [10], no photoexcitation occurs at 355 nm even on the Si substrate surfaces. Photoabsorption of Si is not involved in photolysis of TMGa on Si substrate. This result is not in agreement with the reported enhancement of the photoexcitation of XeF_2 on Si surface.[11] TMGa interacts only slightly with the Si surface whereas F atoms interact strongly with the substrate.

When the substrate temperature was kept at 170 k, a monolayer of TMGa is formed on Si. He I line (58.4 nm) is used as a photolysis light source. Drastic change in UPS spectra were observed as shown in Fig. 7. The signals at 3.8 and 9 eV that are assigned to the Ga-C and C-H bonds became weak. XPS measurement suggests that the ratio of I_C/I_{Ga} is 2.3. Since the excess energy ($hw-D_o$) is as large as 20 eV, CH_3 photofragments may fly away from the substrate surface.

[1] D. J. Ehrlich and R. M. Osgood Jr., Chem. Phys. Lett., 79, 381 (1981) .
[2] J. M. McCaulley, V. R. McCrary, and V. M. Donnelly, J. Phys. Chem., 93, 1148 (1989).
[3] J. Nishizawa, H. Abe, T. Kurabayashi, N. Sakurai, J.Vac.Sci.Technol., A4, 706 (1986).
[4] A. Doi, Y. Aoyagi, S. Namba in Photon, Beam, and Plasma Stimulated Chemical Processes at Surfaces, edited by V. M. Donnelly, I. P. Herman, and M. Hirose (Mater. Res. Soc.,75, Pittsburgh, PA 1987) p.217.
[5] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulser and G. E.Muilenberg, "Handbook of X-ray photoelectron spectro- scopy" (Perkin-Elmer Co., 1978)
[6] G. E. Rhead, J. Vac. Sci. Technol.,13, 603 (1976).
[7] D. Bolmont, P. Chen, C. A. Sebenne and F. Proix, Surf. Sci., 137, 280 (1984).
[8] F. Steinbach, J. Kiss, and R. Krall, Surf. Sci., 157, 401 (1985).
[9] F. Lee, A. L. Backman, R. Lin, T. R. Gow, and R.I. Masel, Surf.Sci., 216, 173 (1989)
[10] M. Sasaki, Y .Kawakyu and M. Mashita, Jpn. J. Appl. Phys., 28, L131(1989).
[11] F.A. Houle, J.Chem.Phys., 80,4851(1985)
[12] C. D. Stinespring and A. Freedman, Appl. Phys. Lett., 52, 1959 (1988).

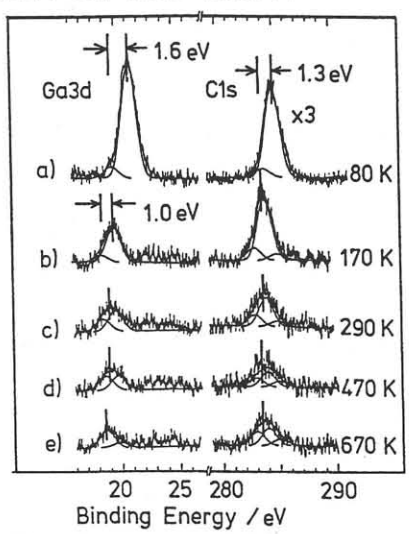

Fig. 1. XPS spectra observed in pyrolysis of TMGa on a Si(111) wafer.

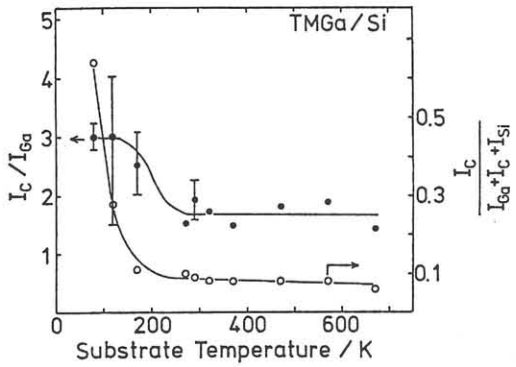

Fig. 2 Temperature dependence of carbon concentration and carbon to gallium ratios from TMGa on Si(111)

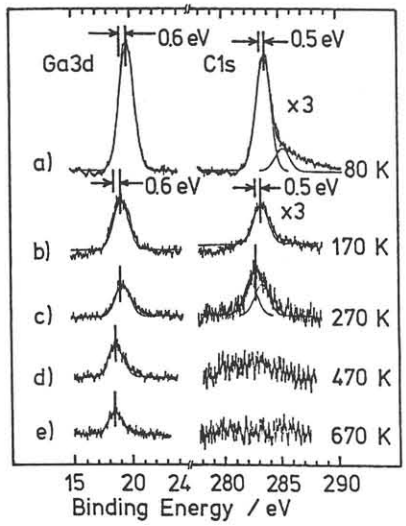

Fig. 3. XPS spectra observed in pyrolysis of TMGa on a polycrystalline Au substrate.

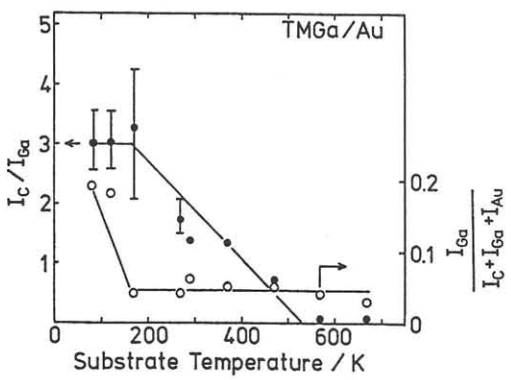

Fig. 4. Temperature dependence of gallium concentration and carbon to gallium ratios from TMGa on Au

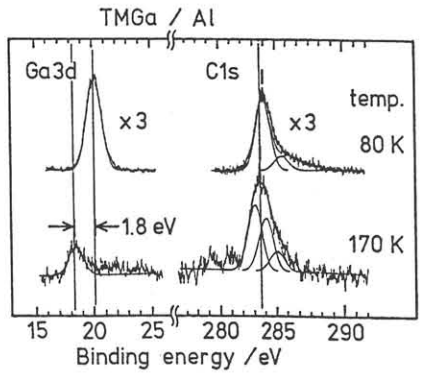

Fig. 5. XPS spectra observed in adsorption of TMGa on a polycrystalline Al substrate.

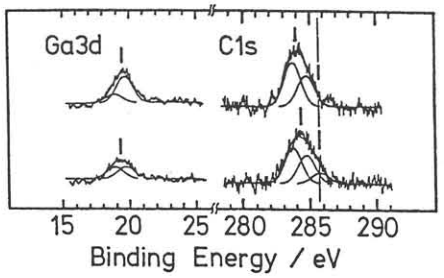

Fig. 6. XPS spectra observed in photolysis of TMGa on Si at 270 K.
(upper) before irradiation,
(lower) after irradiation at 266 nm.

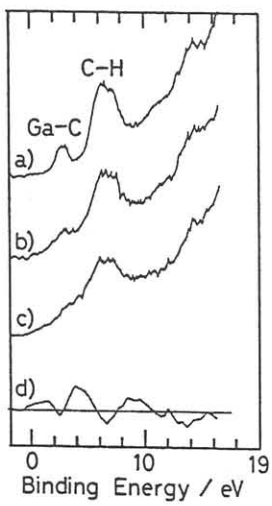

Fig. 7. UPS spectra observed in photolysis of TMGa at 58.3 nm at 170 K.
a) before irradiation
b) after 30 min. irradiation
c) sfter 1 hr. irradiation
d) difference spectrum