

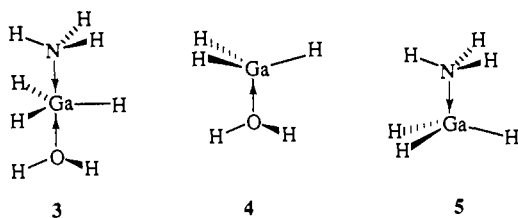
Adsorption of Gallane on Oxidized Silicon

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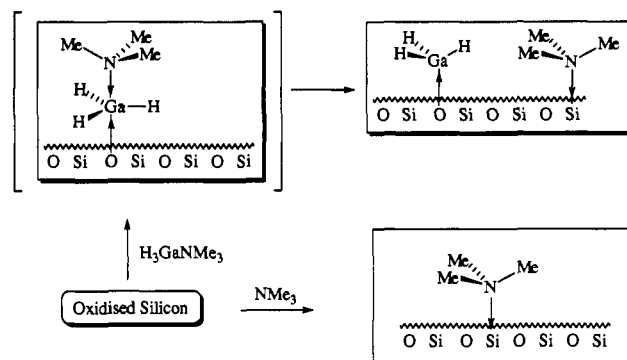
Volatile tertiary amine adducts of gallane are of interest as sources of gallium in chemical vapor deposition technology.^{1–3} These compounds are less developed than related alane adducts, which have similar physical properties but higher thermal stability, and have been shown to be excellent precursors for forming pure aluminum metal films using thermolytic degradation techniques;^{4–8} metal hydrides are devoid of direct metal–carbon interactions and are therefore less susceptible to forming carbonaceous material than metal alkyl species.⁹ Rigorous studies on the adsorption and thermal degradation of the trimethylamine adduct of alane, H_3AlNMe_3 (**1**), on silicon, silicon oxide, aluminum, and gallium arsenide have been reported,^{4–8,10} affording much information on the nature of the species initially adsorbed on the surface. The resulting model for adsorption on silicon oxide¹⁰ has chemical precedence and is supported by theoretical studies. Herein we report our findings on the adsorption of trimethylamine–gallane, H_3GaNMe_3 (**2**), and for comparison NMe_3 , on thermally grown silicon oxide on silicon wafers using X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectroscopy (SSIMS). This includes theoretical studies on $\text{H}_3\text{GaNH}_3(\text{OH}_2)$ (**3**) and H_3GaOH_2 (**4**) as model species for the adsorption of **2**



to surface oxygen centers and, for comparison, theoretical studies on H_3GaNH_3 (**5**). The findings differ dramatically from those obtained for the adsorption of the aluminum analogue, **1**, on the same substrate.¹⁰

Dosing experiments¹¹ are summarized in Scheme I. Compound **2** was prepared from lithium gallium hydride and trimethylamine

Scheme I



hydrochloride and purified by sublimation.¹⁴ The substrate was silicon oxide (500–5000 Å) thermally grown on silicon. This was cleaned by rinsing in acetone, air-dried, and then Ar^+ or Xe^+ beam etched for 20 min ($3\text{-}\mu\text{A}$ ion current) with a preetching pressure of $\leq 3 \times 10^{-8}$ mbar. SSIMS surveys of the etched surface showed a trace of hydroxyl groups (SiOH , $M^+ 45$) and some adventitious carbon (*ca.* 3–4%); after *ca.* 15 min there was a substantial buildup of the hydroxyl groups,¹⁵ along with carbonaceous material, and thus dosing was carried out immediately after etching. Predosing pressure was *ca.* 3×10^{-8} mbar, with dosing pressures of 5×10^{-8} – 5×10^{-7} mbar for 5 min.

Key features of the results include the following. The adsorbed material was gallium rich, Ga:N ratio close to 3:1, with an estimated film thickness¹⁶ of *ca.* 3 Å; note that an absence of nitrogen or gallium on the surfaces prior to dosing meant the ratio of Ga to N was an informative guide to the composition of the deposited material. The Ga $2p_{3/2}$ photoelectron peak was axially symmetric and centered at a binding energy of 1119.8 eV,

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- (11) The experiments were performed under ultrahigh-vacuum using a Perkin-Elmer PHI Model 560 surface analysis system. This system contains a double-pass CMA (Model 25–270 AR) with a perpendicularly mounted dual anode (Mg/Al) X-ray source operated at 500 W. Two Mg $K\alpha$ X-ray sources were operated, each at 250 W. The maximum energy resolution of the CMA was 1.2 eV operated for XPS analysis in the fixed analyzer transmission (FAT) mode with a pass energy of 25 eV for the Ag $3d_{5/2}$ emission. The electron binding energies (E_B) were calibrated against the Au $4f_{7/2}$ emission at $E_B = 84$ eV.¹² The exposure rate was measured in langmuirs (L); 1 L = 1-s exposure at 1.0×10^{-6} mbar. Charging was referenced to the Si $2p$ photoelectron peak from SiO_2 at 103.8 eV.¹³
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- (16) XPS can be used to estimate film thickness by quantifying the attenuation of a characteristic substrate peak by a thin uniform overlayer of a known material. The film thickness, d , is given by $d = \Gamma \ln(I_0/I)$ where Γ is the electron mean free path in the overlayer and I and I_0 are the intensities of a characteristic peak from a covered substrate and a clean substrate, respectively. The accuracy of this technique depends on two factors, the accuracy of the electron mean free path and the uniformity of the overlayer. A nonuniform overlayer will give substrate peaks dominated by contributions from the thinnest portions of the film due to the exponential thickness/peak intensity relationship, as is the case here.¹⁷
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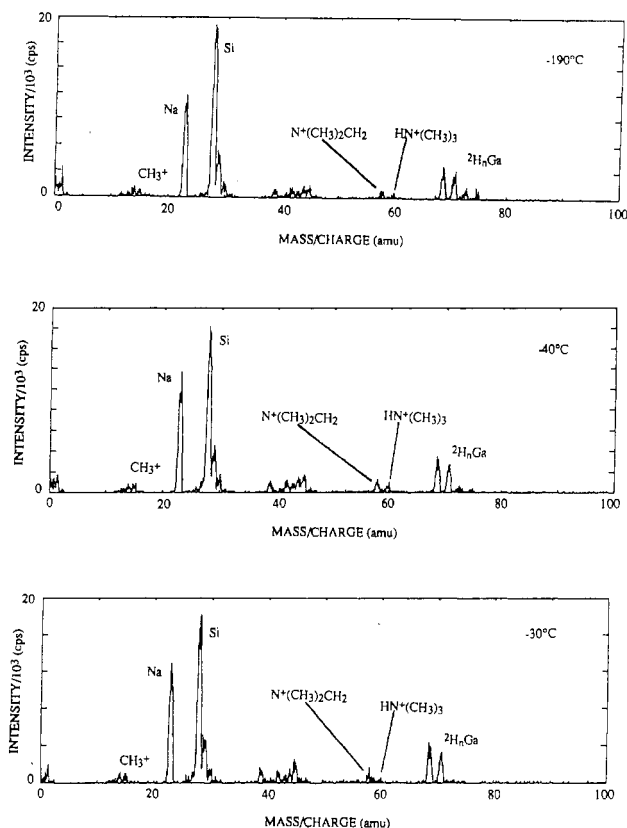


Figure 1. SSIMS surveys of oxidized silicon dosed with H_3GaNMe_3 at -196 , -40 and -30 °C. Note: Sodium is an impurity commonly found on silica (quartz) and oxidized silicon surfaces. SSIMS is, inherently, highly sensitive to alkaline metals, resulting in strong signal intensities for trace amounts (sodium was not detected using XPS).

consistent with a Ga^{III} species, including the presence of Ga–O bonds.¹⁸ The N 1s photoelectron peak ($E_B = 400$ eV) was also axially symmetric, and the peak position and intensities for dosing with **2** and NMe_3 were the same, indicating that **2** dissociates on adsorption with amine binding to surface silicon sites (*viz.* silicon of siloxane bridges). Experiments where the surface was dosed with **2** prior to dosing with NMe_3 (or conversely) resulted in no change to the adsorbed species, indicating that the preadsorbed material occupies and/or successfully conceals all the available binding sites for free amine. The C 1s photoelectron peak was broad and showed multiple species character; the adventitious carbon was readily distinguished from adsorbed carbon containing species using angular-dependent XPS.

SSIMS was used to further investigate the nature of the adsorbed species. For dosing experiments carried out at room temperature (*ca.* 20 °C in the vacuum chamber), SSIMS on **2** and $^2\text{H}_n\text{GaNMe}_3$ confirmed the presence of Ga and NMe_3 on the surface. When dosing of these compounds was carried out at reduced temperature (*ca.* -190 °C) however, $^1,^2\text{H}_n\text{Ga}$ ($n = 0, 1, 2$) and NMe_3 species were evident (Figure 1). No changes in the XPS spectra of both compounds on the surface were observed for the experiments carried out at reduced temperature relative to those at room temperature. It is possible that the absence of H_3Ga and H_nGa species above -40 °C is due to facile Ga–H cleavage using this technique.

In summary, the results for dosing at -190 °C (and above -40 °C) are consistent with dissociative adsorption of **2**, with H_3Ga binding to oxygen centers, and NMe_3 binding to silicon centers, (Scheme I) essentially as a submonolayer. This is in contrast to

the molecular adsorption of the corresponding aluminum analogue, **1**, under the same conditions, which yielded a five-coordinate species, $\text{H}_3\text{Al}(\text{NMe}_3)(\text{O}=\text{O})$, at low dosing pressures, and with further uptake of alane under high dosing pressures, affording a hydride bridged species, $\text{H}_2(\text{NMe}_3)\text{Al}(\mu\text{-H}_2)\text{AlH}_2(\text{O}=\text{O})$.¹⁰ In addition, for the alane system there is a high-energy X-ray-induced migration of NMe_3 groups from $\text{H}_3\text{Al}(\text{NMe}_3)(\text{O}=\text{O})$ to silicon, with the resulting Al:N ratio associated with Si-bound NMe_3 groups approximately 3:1, as for the Ga:N in the present study. This finding alone supports that the binding of NMe_3 in the present case is to the silicon centers, and that the formation of hydride bridging species similar to those postulated to account for the high Al:N ratio at high dosing pressures of H_3AlNMe_3 , can be ruled out. Indeed, in the present study there was no apparent secondary adsorption process at high dosing pressures, and any X-ray damage to the adsorbed species is restricted to Ga–H bond scission, which is likely given the frailty of such bonds. The difference in adsorption characteristics of **2** and H_3AlNMe_3 is in accordance with the weaker nature of both Ga–H and Ga–N bonds and with gallane preferentially forming stable four coordinate species with Lewis bases (see below) whereas alane can form four- or five-coordinate species, including hydride bridges,¹⁹ or even cationic six-coordinate species.²⁰

The formation of a five-coordinate intermediate species $\text{H}_3\text{Ga}(\text{NMe}_3)(\text{O}=\text{O})$ with the hydrides in the trigonal plane of a trigonal bipyramidal metal environment may be the primary process of adsorption of **2** (Scheme I). Such a species would be short-lived, rapidly losing NMe_3 . This is consistent with the existence of a five-coordinate bis(trimethylamine)–gallane species below *ca.* -26 °C²¹ and theoretical considerations on model species. *Ab initio* molecular orbital calculations on **3–5** were at the STO-3G, 3-21G*, and HF/D95*+DZP²² level using Gaussian 90.²³ For H_3GaNH_3 the Ga–N distance, 2.193 Å, is significantly longer than those in structurally authenticated tertiary amine adducts of gallane, 2.085(3) and 2.094(4) Å, in $[(\text{H}_3\text{GaNMe}_2\text{CH}_2)_2]^{3,24}$ and 2.063(4) Å in $\text{H}_3\text{GaN}(\text{CH}_2\text{CH}_2)_3\text{CH}_3$.³ Nevertheless at this level of theory the results provide a relative comparison between the three model species. The stabilization energy of $\text{H}_3\text{GaNH}_3(\text{OH}_2)$ relative to H_3GaNH_3 and OH_2 is only 0.67 kcal mol⁻¹ (considerably less than that for the alane system, 4.71 kcal mol⁻¹), which is consistent with the inherent instability of five-coordinate gallane species.²¹ Conversion of $\text{H}_3\text{Ga}(\text{NH}_3)(\text{OH}_2)$ to H_3GaOH_2 and free amine requires 7.8 kcal mol⁻¹, which is a relatively low-energy process and is consistent with cleavage of the Ga–N bond on adsorption of **2** to surface O centers. Moreover, this is significantly less for the alane system, 13.16 kcal mol⁻¹, where the five-coordinate species prevails at ambient temperature on dosing with H_3AlNMe_3 .¹⁰

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Supplementary Material Available: A table of optimized computed geometries and energies and a figure showing the structures for $\text{H}_3\text{Ga}(\text{NH}_3)(\text{OH}_2)$, H_3GaOH_2 , and H_3GaNH_3 (3 pages). Ordering information is given on any current masthead page.

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