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Author(s)	Sano, H.; Sakai, J.; Mizutani, G.; Ushioda, S.
Citation	Journal of Electron Spectroscopy and Related Phenomena, 64-65: 865-870
Issue Date	1993
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/4407
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Description	

Raman Scattering from Trimethylaluminum (TMA) : Free and Adsorbed Molecules on GaAs(100)

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We have measured the Raman scattering from an adsorbed layer of trimethylaluminum (TMA) on GaAs(100) as a function of coverage down to 17 monolayers. The absolute scattering cross-section of the CH_3 -symmetric stretching mode of TMA was found to be $8.0 \times 10^{-29} \text{ cm}^2/\text{dimer sr line}$. The corresponding cross-section in the gaseous state is $2.6 \times 10^{-29} \text{ cm}^2/\text{dimer sr line}$. The observed enhancement of the cross-section in the multilayer is due to the effect of the molecular field. The scattering cross-section of the CH_3 -symmetric stretching mode of gaseous trimethylgallium (TMG) is $1.3 \times 10^{-29} \text{ cm}^2/\text{molecule sr line}$. Based on these data on the absolute Raman cross-sections, we expect that the monolayer of these molecules on GaAs would be extremely difficult to observe by Raman scattering in a crystal growing environment.

1. INTRODUCTION

Trimethylaluminum (TMA) and trimethylgallium (TMG) are important source molecules used in the growth of GaAs and AlAs crystals by metalorganic chemical vapor deposition (MOCVD). Although both the standard CVD and atomic layer epitaxy (ALE) methods are often used in growing GaAs and AlAs using these gases, the details of the atomic reaction processes involved in the growth mechanism are not well understood. If one can observe the vibrational spectra of these molecules when they are adsorbed on a growing surface of GaAs or AlAs crystals, one can investigate the atomic and molecular dynamics of crystal growth in situ. To make such studies possible, the Raman signal from surface adsorbed molecules must be sufficiently large for the observation of a monolayer. With this application of Raman spectroscopy in mind, we have been investigating the absolute Raman scattering cross-sections of TMA and TMG both in the free gaseous state and the adsorbed state on GaAs(100).

In our previous work we determined the absolute Raman cross-sections of TMA and TMG in the gaseous state [1]. In the present work we

have determined the absolute cross-section of a multilayer of TMA molecules adsorbed on the GaAs (100) surface.

2. EXPERIMENT

The substrate was a Si doped n-type GaAs single crystal with a carrier concentration of $1.9 \times 10^{19} \text{ cm}^{-3}$. Its mirror-like (100) surface was cleaned initially in air by the following procedure. The first step of cleaning was done by methanol and acetone, and then it was etched in a mixture of $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O}$ (5 : 1 : 1) at 60°C for 60s. After removing the etching solution by rinsing with purified water, the substrate was immersed in a solution of $(\text{NH}_4)_2\text{S}_x$ with $x > 1$. By this procedure a thin oxide layer on the GaAs surface is removed and a layer of sulfur is deposited [2]. The sulfur layer protects the surface against oxidation in air.

After placing the GaAs substrate in an ultra-high vacuum (UHV) chamber with a base pressure of 3×10^{-10} torr, the sample was heated to remove the sulfur layer. The Auger spectrum of the cleaned surface indicates that the residual oxygen is below the detection limit and that

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carbon and sulfur are barely detectable. This level of carbon and sulfur does not affect the present experiment. The subsequent adsorption of TMA and Raman scattering measurements were done in this UHV environment.

The TMA molecules were adsorbed on the GaAs surface by cooling the substrate below 158 K and back-filling the chamber with the vapor of TMA at a pressure of $1 - 4 \times 10^{-6}$ torr. Cooling of the substrate was necessitated by the fact that no more than a single monolayer of TMA adsorb on the GaAs surface at room temperature. The film thickness of TMA was calibrated in situ simultaneously with the Raman measurement by measuring the reflectivity of the film as a function of the exposure and by fitting the data with a theoretical curve. The theoretical curve was calculated for a three-layered structure that consists of GaAs, TMA film, and vacuum [3]. It was calculated for the s-polarized incident light at 488.0 nm with the incident angle of 24° . Then the fitting parameters are the film thickness t and the dielectric constant of the film ϵ .

We needed to determine the film thickness by this reflectivity method rather than by simply calibrating the thickness against exposure, because the proportionality factor between the film thickness and exposure could not be determined consistently for different runs. In connection with this problem, we were surprised by the extraordinarily high level of exposure required to deposit a sufficient number of TMA molecules to be detected by Raman scattering. (See the exposure scale in Fig. 2.) To see what molecules are actually present in the chamber when the TMA gas is leaked into it, we analyzed the gas in the chamber with a quadrupole mass analyzer. The result shows that immediately after the TMA container is initially opened to the chamber much of the gas that exists in the chamber consists of CH_3 and CH_4 . Evidently a large fraction of the TMA molecules decomposes as they strike the walls of the chamber. Thus the partial pressure of TMA is only a small fraction of the total pressure read by the ion gauge. This fact explains why an unusually large amount of apparent exposure is required before the Raman signal from TMA becomes detectable. We found the thickness determined from the reflectivity is reliable and repro-

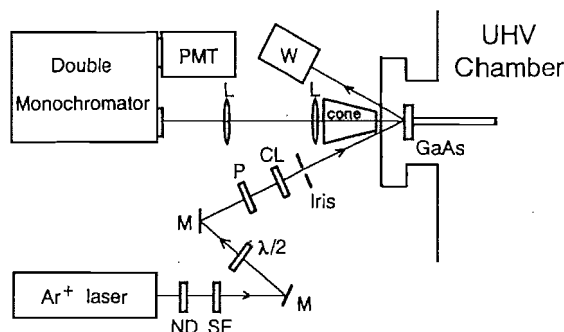


Figure 1: Experimental setup for Raman scattering from an adsorbed layer in UHV. ND: neutral density filter; SF: spike filter; $\lambda/2$: half wave plate; P: polarizer; CL: cylindrical lens; L: lens; M: mirror; W: power meter; PMT: photomultiplier.

ducible.

The Raman measurements were performed by the experimental setup illustrated in Fig. 1. The incident light was the 488.0 nm line of an argon ion laser at a power level of 50 mW. The incident angle was 24° from the surface normal and the polarization was perpendicular to the plane of incidence (s-polarized). The scattered light was collected in the direction of the surface normal without a polarization analyzer. A blackened cone was placed in front of the collection optics to reject diffuse scattered light from the sample surface and the window. The solid angle of collection was $\Delta\Omega = 2.84 \times 10^{-2}$ sr.

The spectrometer was a double grating Czerny-Turner type (Jobin-Yvon, U-1000), and the photomultiplier was a blue sensitive tube (Hamamatsu Photonics, R649) with a very low dark count rate. The absolute sensitivity of this spectrometer system was calibrated earlier as a function of wavelength and polarization by using a standard halogen lamp [4]. Thus the photon counting rate can be directly converted to absolute intensity.

The absolute Raman intensity measurement for the cross-section determination was done for the symmetric stretching mode of the methyl group whose frequency is $\sim 2900 \text{ cm}^{-1}$. From the entire spectrum of the adsorbed TMA layers, we

confirmed that the adsorbed layers consist of the dimers of this molecule [1].

We also carried out a Raman experiment to determine the lower limit of the number of adsorbed layers that can be detected by our spectrometer system. For this measurement the exciting beam was p-polarized and incident along the direction 60° from the surface normal. The incident power was limited to 160 mW to avoid desorption of TMA by heating. The scattered light with p-polarization was collected in the direction 60° from the surface normal. This scattering configuration was theoretically found to be optimum for film thicknesses below 300 \AA , because the electric field in the TMA layer becomes maximum [5].

3. RESULTS

Fig. 2 shows the dependence of the Raman intensity of the 2900 cm^{-1} line of TMA and the reflectivity of the film both as a function of exposure. (As we have noted earlier, the exposure determined from the total pressure measurement is much greater than the actual exposure of TMA.) The reflectivity is shown in the upper panel where the open circles are the data points and the solid curve is the theoretical fit. The oscillation in the reflectivity is caused by the interference effect in the film. The dielectric constant of GaAs was taken to be $\epsilon(488.0 \text{ nm}) = 20 + i3.9$ [6]. By fitting the data with the theoretical curve, we determined the film thickness that corresponds to the exposure and the dielectric constant of the film ($\epsilon = 2.4$). The thickness calibration is shown at the top of the upper panel.

The Raman intensity as a function of coverage is plotted by open circles in the lower panel. The solid curve is a theoretical fit. We will discuss the method and the parameters used in calculating this curve in the next section. We note that the Raman intensity does not increase monotonically with increasing exposure; there is a local minimum around 1700 \AA . This minimum corresponds to the local maximum of the reflectivity. The Raman intensity decreases here, because the penetration of the incident light into the TMA layer has a local minimum at this thickness.

Fig. 3 shows the Raman spectra for the low end of the coverage for which the signal could be

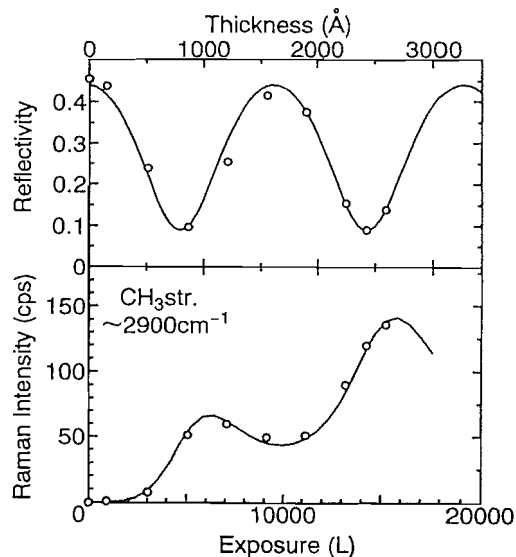


Figure 2: Reflectivity and Raman intensity of a multilayer of TMA on GaAs(100) as a function of exposure and layer thickness. The open circles are the data points and the solid curves are the theoretical calculations. See the text about the unusually high exposure.

observed. The Raman peak at 2890 cm^{-1} could be observed above the exposure of 650 L. The peak intensity at this exposure was ~ 4 cps and the integrated intensity was ~ 6 cps. Assuming that the thickness calibration for this separate run is approximately the same as for the result shown in Fig. 2, the thickness that corresponds to 650 L is $65\text{--}110 \text{ \AA}$ or $12\text{--}21$ monolayers. This is the first time that the Raman spectra of adsorbed TMA was observed. There are examples of infrared observation of TMA on GaAs [7,8].

4. DISCUSSION

4.1. Absolute Raman cross-section of adsorbed TMA

We first describe the theoretical method by which the fitting of the Raman and reflectivity data in Fig. 2 was done and how the absolute Raman scattering cross-section was obtained by the fitting procedure. The Raman scattering intensity from an adsorbed layer on a substrate is

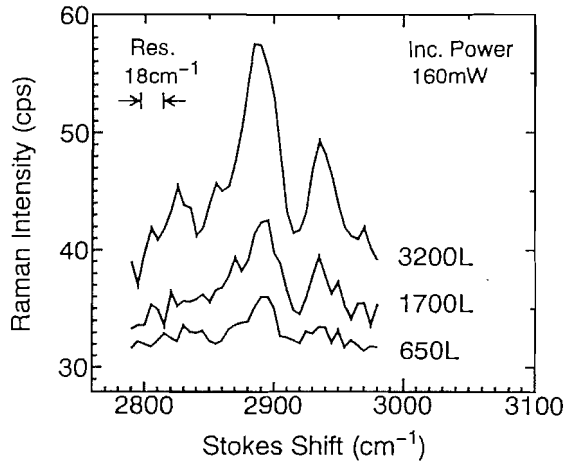


Figure 3: Raman spectra of multilayers of TMA on GaAs for different exposures. The spectra show only the relevant portion for the symmetric stretching mode of the methyl group.

given by:

$$N_{obs}(t) = \left(\frac{d\sigma}{d\Omega}\right)_{ad} N_L \gamma(t) \rho_s(t) \Delta\Omega \eta_{sys} \quad (1)$$

where $(d\sigma/d\Omega)_{ad}$ is the absolute Raman scattering cross-section of the adsorbate in the unit of $\text{cm}^2/\text{dimer sr line}$. This is the parameter to be determined by fitting the data of Fig. 2. N_L is the number of incident photons per second, which is 1.2×10^{17} photons/s (488.0 nm, 50 mW) in the present experiment.

$\gamma(t)$ is the factor that accounts for the effect of the substrate on the incident and scattered electric fields. This factor is calculated by using the electromagnetic Green's function for the three layered structure that consists of GaAs, TMA film, and vacuum above. The calculation method has been described previously by us [5]. For this calculation we used the dielectric constants of the media, $\epsilon(\text{GaAs}, \lambda_{in}) = 20 + i3.9$, $\epsilon(\text{GaAs}, \lambda_{sc}) = 16 + i2.1$, and $\epsilon(\text{TMA}) = 2.4$. The value of $\gamma(t)$ varies with the film thickness t . For example its value is 1.2 at $t = 100$ nm.

$\rho_s(t)$ is the surface density of the TMA molecules. This parameter was calculated from the film thickness t by assuming that the density is equal to that of the liquid TMA, which is $3.14 \times$

10^{21} dimers/ cm^3 . Then $\rho_s(t) = (3.14 \times 10^{21}) \times t$ dimers/ cm^2 . $\Delta\Omega$ and η_{sys} are the solid angle of collection and the efficiency of the spectrometer system, respectively. The system efficiency is 9.33×10^{-3} including the photomultiplier efficiency at the wavelength of the scattered light (568.4 nm).

The solid theoretical curve in the lower panel of Fig. 2 was obtained by Eq. (1). We see that the fit is excellent and that this theory properly explains the unusual variation of the scattered intensity as a function of the film thickness. The single fitting parameter is the absolute Raman cross-section, namely the scale of the vertical axis. As a result of this fitting procedure we obtained the value of the absolute cross-section:

$$\left(\frac{d\sigma}{d\Omega}\right)_{ad} = 8.0 \times 10^{-29} \text{ cm}^2/\text{dimer sr line} \quad (2)$$

To be precise, this cross-section is the component parallel to the surface, $(d\sigma_{XX}/d\Omega)$ and $(d\sigma_{YY}/d\Omega)$ where X and Y are the directions parallel to the surface. If the TMA molecules are oriented randomly and the film is isotropic, $(d\sigma_{ZZ}/d\Omega)$ also has the same value.

In our previous work [1] we obtained the absolute Raman cross-sections of the gaseous TMA and TMG. The cross-section for the symmetric stretching mode of these molecules are:

$$\left(\frac{d\sigma}{d\Omega}\right)_{TMA,gas} = 2.6 \times 10^{-29} \text{ cm}^2/\text{dimer sr line} \quad (3)$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{TMG,gas} = 1.3 \times 10^{-29} \text{ cm}^2/\text{molecule sr line} \quad (4)$$

By comparing Eq. (2) and (3) we see that the cross-section for the multilayer film of TMA is 3.1 times greater than that of the TMA gas. We believe that this difference arises from the difference between the macroscopic field and the molecular field. This effect will be discussed in the following section.

4.2. The effect of the molecular field

The cross-section we have just obtained is defined with respect to the macroscopic electric

field. However, the electric field that is felt by the molecule in a film is the molecular field [9]. The field felt by the molecule in a gaseous state is equal to the macroscopic field, because the neighboring molecules are far apart. Thus when we compare the cross-sections of the same molecule in the gaseous state and in a film, we must take into account the difference between the macroscopic and molecular fields. The molecular field \mathbf{E}_m is in general greater than the macroscopic field. Thus the cross-section for the molecule in a film will appear to be greater than that in a gas.

The strength of the molecular field depends on the details of the environment in which the molecule is placed. The usual way to estimate it is to assume that the molecule lies in a microscopic cavity of the spherical shape carved out of the material in which it is placed. Under this approximation the molecular field is given in terms of the macroscopic field \mathbf{E} by:

$$\mathbf{E}_m = \frac{(\epsilon + 2)}{3} \mathbf{E} \quad (5)$$

where ϵ is the dielectric constant of the medium. If we use the value of the dielectric constant of the TMA film, $\epsilon = 2.4$ in Eq. (5), we find that the molecular field is 1.47 times the macroscopic field. Since the Raman intensity is proportional to the fourth power of this factor, we expect the enhancement of the Raman intensity due to this effect to be 4.6 times. This factor is comparable to the observed factor of 3.1.

The TMA molecule is a planar molecule with three methyl groups lying in a plane. Thus it may be more appropriate to consider the molecular field in a cavity with a flat disk shape. Then the molecular field parallel to the flat faces of the disk can be calculated:

$$\mathbf{E}_m = \left(1 + \frac{h(\epsilon - 1)}{2\sqrt{h^2 + d^2}}\right) \mathbf{E} \quad (6)$$

where d and h are the diameter and the height of the disk, respectively. If we take the ratio between d and h to be $d/h = 1.9$, we can reproduce the measured enhancement factor of 3.1. Since the incident light was s-polarized, the electric field is parallel to the surface. Thus the above result may be interpreted to imply that the planar TMA dimers are stacked parallel to the surface.

However, we must be cautious in accepting this conclusion, because this line of reasoning contains many assumptions.

The increase in the apparent cross-section as a molecule goes from the gaseous state to a liquid state has been observed in other examples [10,11]. In these cases also the effect of the molecular field was considered as the cause of the increase in the scattered intensity. We believe that it is reasonable to assume that the intrinsic molecular cross-section is unchanged for the adsorbed TMA relative to the free TMA, because TMA is physisorbed on GaAs. Thus there is little change in the molecular orbitals of TMA upon adsorption.

4.3. Possibility for observing a monolayer of TMA on GaAs

Based on the absolute cross-sections obtained above, we estimate the Raman scattering intensity from a monolayer of TMA on GaAs, and examine the possibility of observing the Raman spectra in situ in a crystal growing environment. We use Eq. (1) with appropriate realistic experimental parameters. For $\Delta\Omega$ and η_{syy} , we use the same values used in this work, namely $\Delta\Omega = 2.8 \times 10^{-2}$ sr and $\eta_{syy} = 9.33 \times 10^{-3}$. The incident power is assumed to be 500 mW at 488.0 nm which corresponds to $N_L = 1.2 \times 10^{18}$ photons/s. According to a published result [12], there are three distinct adsorption sites for TMG on GaAs, and the total surface density of the first monolayer is 3.4×10^{14} molecules/cm². This value is very close to the estimate obtained by taking the 2/3 power of the density of the liquid TMG. There are no published data on the surface density of TMA on GaAs. For this value we will use the estimate from the liquid TMA density which is 1.7×10^{14} dimers/cm².

There is some ambiguity in estimating the value of γ , because we do not know the dielectric constant of the monolayer ϵ_{ad} . Thus we will take the two extreme cases $\epsilon_{ad} = 1$ for zero screening and $\epsilon_{ad} = 2.4$ for full screening by the adsorbed monolayer. We obtain the maximum and minimum estimates, corresponding to these values of ϵ_{ad} . The calculation was carried out for p-polarized incidence at 60° and the scattering an-

gle of 60° both from the surface normal. The Raman intensities calculated by the above assumptions are:

$$N_{obs} = \begin{cases} 2.8 \text{ cps} & \text{for } \epsilon_{ad} = 1.0 \\ 0.1 \text{ cps} & \text{for } \epsilon_{ad} = 2.4 \end{cases} \quad (7)$$

The maximum intensity is expected when there is no screening of the electric fields due to the adsorbed layer itself, i. e. when $\epsilon_{ad} = 1$. Empirically, the fluctuation in the background intensity for the incident power of 500 mW is about 1 cps. Thus the Raman spectrum is observable when the upper limit of the estimate (2.8 cps) is applicable, but it will be difficult to observe if the lower limit is taken. Even if a similar molecular field enhancement factor to the present result (~ 3.1) exists, it will require an improvement of the spectrometer system efficiency of a factor 4 to observe the monolayer. However, it is difficult to imagine that the molecular field effect is strong for a monolayer.

5. CONCLUSIONS

We have determined the absolute Raman scattering cross-section of a multilayer of TMA adsorbed on GaAs. It is apparently enhanced relative to the cross-section of the gaseous TMA. We believe the enhancement is due to the effect of the molecular field. The estimate for the Raman intensity of TMA on GaAs indicates that it is extremely difficult to observe a monolayer under realistic conditions in a crystal growing environment.

ACKNOWLEDGEMENTS

We thank Fujitsu Laboratories, Ltd. for providing financial and materials support. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

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