

## Photodesorption and Photodissociation of OCS on GaAs(100)

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Adsorption of OCS on GaAs(100) has been investigated using temperature-programmed desorption and photoinduced desorption/dissociation spectroscopy. It was observed that OCS molecularly adsorbs on GaAs(100) and thermally desorbs at 160 K. Adsorbed OCS molecules either dissociate into gaseous CO, leaving S adsorbed on GaAs(100), or desorb as molecular OCS under irradiation of  $\lambda = 300 \sim 770$  nm. The photodissociation cross section is about  $5.0 \times 10^{-19}$  cm<sup>2</sup> at 300 nm, which is about 2 orders of magnitude higher than that for gaseous OCS at 250 nm and even 10 times greater compared with that for OCS on Ag(111) at 254 nm. It drops rapidly as the wavelength increases and becomes undetectable at about 480 nm. In addition, the photodesorption cross section was found to be about  $8.4 \times 10^{-20}$  cm<sup>2</sup> at 300 nm with a threshold at about 770 nm. We also observed that the photodissociation cross section is strongly dependent on the coverage of OCS on GaAs(100), changing from  $2.0 \times 10^{-18}$  cm<sup>2</sup> for 0.03 L OCS on GaAs(100) at 320 nm to  $3.6 \times 10^{-19}$  cm<sup>2</sup> for 3.3 L OCS. A 2.4 eV red shift of threshold photon energy for photodissociation of OCS on GaAs(100) was observed in our experiment relative to gaseous OCS. Our results support the interaction of photogenerated carriers with adsorbed OCS in the photochemical processes. The observed difference in the threshold energies for photodissociation and photodesorption is possibly attributable to the different final states involved.

### Introduction

Gallium arsenide devices are known to be faster and consume less power for the same speed compared to silicon.<sup>1</sup> However, with all these advantages, GaAs has a serious problem: it suffers from a surface effect known as Fermi-level pinning. Extensive work dealing with the passivation of GaAs surfaces has been carried out.<sup>1–11</sup> Sandroff et al. reported a 60-fold increase in current gain of GaAs heterojunction bipolar transistors when the devices were spin coated with thin films of Na<sub>2</sub>S.<sup>9</sup> However, the passivated surface is unstable in air and will be oxidized rapidly. It was found that using H<sub>2</sub>S gives a treated surface that is more stable in air or water.<sup>6</sup> Recently the passivation of the GaAs surface involving gas phase sulfur compounds has attracted considerable attention.<sup>2,3</sup> As part of our attempt to passivate GaAs by gas phase sulfur deposition, the photochemistry of adsorbed OCS on GaAs has been studied.

The photochemistry of OCS, both in gas phase and as adsorbed molecules on substrate surfaces, has been well studied.<sup>11–17</sup> In gas phase, the bond dissociation energies are  $D_0(\text{OC}-\text{S}) = 3.12 \pm 0.03$  eV and  $D_0(\text{O}-\text{CS}) = 6.81 \pm 0.13$  eV.<sup>12</sup> The UV absorption spectrum starts at about 255 nm and maximizes at 225 nm with a cross section of about  $1 \times 10^{-19}$  cm<sup>2</sup>. OCS dissociates into CO and S atom with UV irradiation between 190 and 255 nm. The cross section at 250 nm is about 2 orders lower than that at 225 nm.<sup>11</sup>

Photodissociation of OCS molecules adsorbed on LiF(001) at 222 nm has been reported by Polanyi and co-workers.<sup>14</sup> For low coverage ( $\sim 10^{-4}$  ML), the cross section for photodissociation at 222 nm in the adsorbed state,  $\sigma_{\text{ph}}(\text{ad})$ , was found to be enhanced by  $10^3$ – $10^4$  times relative to the value obtained in the gas phase. In addition,  $\sigma_{\text{ph}}(\text{ad})$  was dependent on the OCS coverage, decreasing as the adsorbate dose, and hence coverage, increased.

The thermal and photoinduced chemistry of OCS adsorbed on Ag(111) at 100 K has been investigated by Zhou and White.<sup>12</sup>

OCS was found to adsorb molecularly at 128 K with no thermal decomposition. Using temperature-programmed desorption (TPD) and Auger electron spectroscopy, the authors found that OCS dissociates into CO, desorbing into gas phase, and adsorbed S, retained on the surface, under full arc irradiation ranging from 230 to 900 nm. The photodissociation cross section was found to be  $\sim 4.4 \times 10^{-20}$  cm<sup>2</sup> at 254 nm. It decreases rapidly with increasing the wavelength. Compared to gas phase photochemistry, the photodissociation of OCS on Ag(111) has a higher cross section and a lower threshold of 430 nm.

In this work, we present the results of the photodissociation of OCS on the GaAs(100) surface at 100 K. TPD and photoinduced desorption/dissociation spectroscopy (PIDS) were employed to study the effects of OCS exposures, irradiation time, photon intensity, and wavelength on the photochemical process. In general, we found trends similar to those obtained for OCS adsorbed on LiF(001) and Ag(111). The photoreaction cross section of OCS on GaAs(100) at 320 nm was observed to decrease with increasing the OCS exposure. It drops from a value of  $2.0 \times 10^{-18}$  cm<sup>2</sup> for 0.03 L of OCS exposure to  $3.6 \times 10^{-19}$  cm<sup>2</sup> for 3.3 L. In addition, our experiment further demonstrates that the photodissociation cross section of OCS on GaAs(100),  $\sigma_{\text{ph}}(\text{ad}) = 5.0 \times 10^{-19}$  cm<sup>2</sup> at 300 nm, is significantly higher than the values in gas phase. In the gas phase, the photodissociation cross section of OCS only exists in the range  $\lambda < 255$  nm and is undetectable at 320 nm. At 250 nm the photodissociation cross section of gaseous OCS is only  $\sim 10^{-21}$  cm<sup>2</sup>. Apart from the enhancement in the photodissociation, we also observed a photodissociation threshold of 480 nm for adsorbed OCS on GaAs(100) that is about 2.4 eV lower than that in gas phase.

### Experimental Section

The experiments were carried out in a stainless steel ultrahigh vacuum chamber equipped with an ion gun for cleaning and a multichannel quadrupole mass spectrometer (MSK PPT). The chamber was pumped by a combination of ion, titanium

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sublimation, and turbo molecular pumps. The base pressure after bake-out is about  $1.6 \times 10^{-10}$  Torr.

The quadrupole mass spectrometer was enclosed by a glass shield with a 3 mm opening in the front to reduce contribution from other components during desorption measurements. During TPD, the sample was positioned about 1 mm away from the opening of the glass shield. A typical TPD spectrum was taken by ramping the temperature at 5 K/s.

The semi-insulating sample (8 mm  $\times$  12 mm) was cut from a commercial GaAs(100) wafer from American Xtal Technologies. The wafer was shipped under dry nitrogen atmosphere. The sample was cut and inserted into the chamber immediately, without chemical cleaning, after the package was opened. It was heated resistively by passing a current through a thin tantalum foil (6 mm  $\times$  12 mm  $\times$  0.025 mm) that was sandwiched between the sample and another small piece of GaAs (6 mm  $\times$  12 mm) cut from the same wafer. They were held together by a pair of small narrow clippers made of elastic stainless steel. Although the clippers occupied a small area of the sample surface, the effective surface area was large enough, and the clippers were verified not to produce any significant noise signal interfering with our measurement. The heating foil was in turn spot-welded to two 1.5 mm diameter tantalum rods which were connected to the electrical feedthrough at the bottom of the cylindrical sample holder. Liquid nitrogen was used to cool the sample to below 100 K.

The temperature of the sample was monitored and controlled by a temperature controller (RHK MODEL 310). It was measured by a C-type thermocouple spot-welded to a small tantalum tab which was attached to the back of the sample with high-temperature ceramic adhesive (Aremco 516).

The OCS used in this experiment was obtained from Matheson with a purity of 97.5%. The gas was introduced into the chamber through a capillary doser with a factor of 33. The exposures were measured in the unit of langmuir (L), equal to  $10^{-6}$  Torr s.

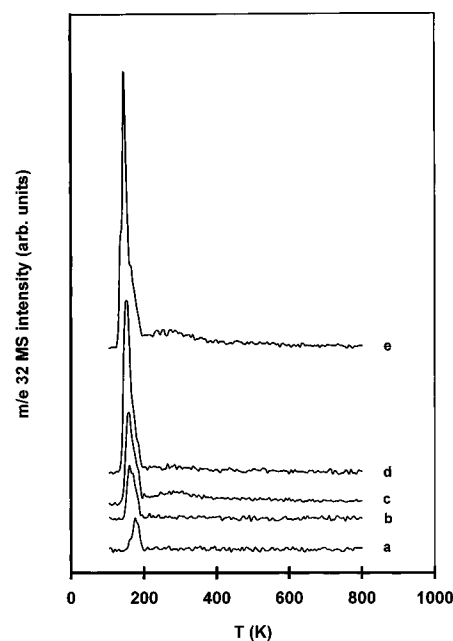
The sample was cleaned by argon ion bombardment (500 eV,  $3 \mu\text{A}/\text{cm}^2$ ) at 300 K for 30 min, followed by annealing at 820 K for 4 min. The ion beam was kept at an incident angle of  $45^\circ$  during the sputtering process. The annealing temperature was not allowed to exceed 850 K so as to keep the surface composition stoichiometric. Such a procedure has been reported in previous work to give a Ga-rich  $c(8 \times 2)$  surface structure.<sup>18</sup> It was repeated to refresh the surface after sulfur deposition.

The photon source used to irradiate the surface is a 1000 W Xe lamp from Oriel that produces light with  $\lambda > 260$  nm. A water filter was installed to remove IR radiation above 900 nm. A lens was used to focus the light onto the crystal surface such that only the effective area of the surface, and no other parts, was irradiated. Long pass filters from Oriel were inserted into the optical path to obtain light beams with various cut-on wavelengths. The cut-on wavelengths of the filters employed were 285, 324, 348, 385, 400, 475, 515, 645, 725, 830, and 850 nm. A 320 nm band-pass filter was also used to generate light with wavelength ranging from 260 to 380 nm. During PIDS, the mass spectrometer was positioned at  $45^\circ$  from the surface normal.

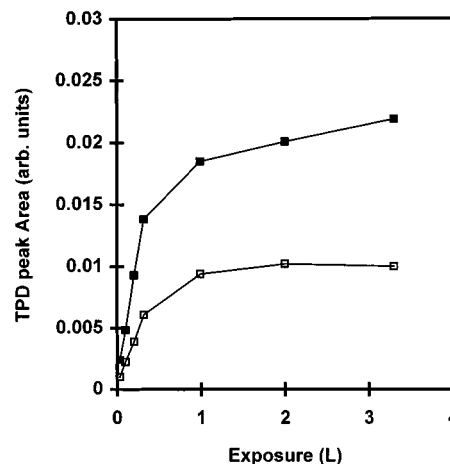
Since the temperature increase during UV irradiation was small, the PIDS signal observed in our work cannot be attributed to the thermal effects. Both the S ( $m/e = 32$ ) and OCS ( $m/e = 60$ ) were followed to monitor the desorption OCS molecules during the photoirradiation or thermal annealing.

## Results

Adsorption and desorption of OCS on GaAs(100) were studied by TPD, and the results are shown in Figure 1. OCS



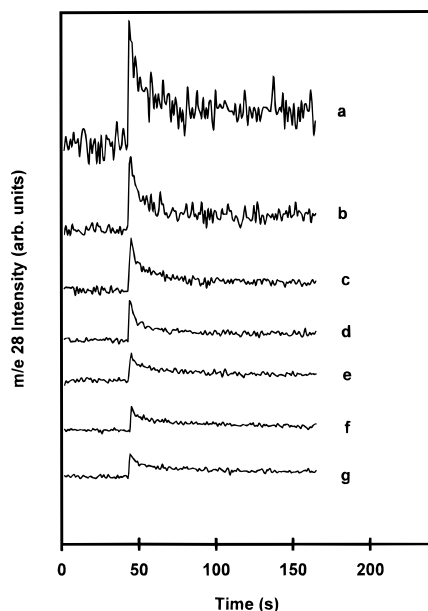
**Figure 1.** TPD spectra of  $m/e = 32$  after exposing OCS to GaAs(100) at 100 K: (a) 0.03, (b) 0.1, (c) 0.2, (d) 0.3, and (e) 1.0 L.



**Figure 2.** Plot of integrated peak area of OCS desorption vs exposure: (■)  $m/e = 32$ , (□)  $m/e = 60$ . The adsorption temperature was 100 K, and the heating rate of 5 K/s was employed in TPD.

was dosed onto the crystal at 100 K with various exposures. Masses 28 (CO), 32 (sulfur), and 60 (OCS) were simultaneously monitored during the thermal desorption, giving identical desorption behavior. Only one desorption peak was observed at 160 K. As the exposure was increased, the peak slightly shifted toward low-temperature. By using the multichannel mass spectrometer, we noticed that in addition to peaking at the same temperature, the ratios between respective mass spectroscopy (MS) signals for  $m/e = 32$ , 28, and 60 approximated the corresponding ratios obtained for background gaseous OCS. This indicates that only molecular OCS desorbs from the surface. The TPD area increases rapidly and linearly with OCS exposure below 0.5 L and reaches saturation at about 1.0 L (Figure 2).

Photoinduced desorption/dissociation spectra were obtained by UV irradiating OCS/GaAs(100) at 100 K at various exposures. At the moment the shutter for UV light was removed, an initial peak in MS signal for  $m/e = 28$  was observed (Figure 3). The UV light applied was centered at 320 nm, ranging from 260 to 380 nm. The PIDS have been weighted by the initial OCS coverage. Hence the spectra presented in Figure 3 reflect the relative possibilities for a single adsorbed

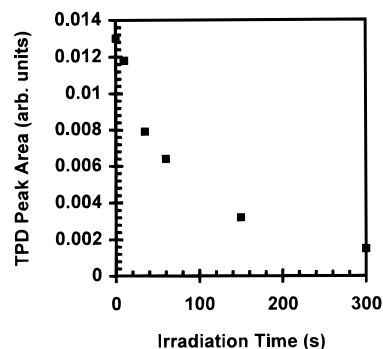


**Figure 3.** Normalized photoinduced dissociation (PID) spectra ( $m/e = 28$ ) of OCS on GaAs(100) at 100 K upon various exposures: (a) 0.03, (b) 0.1, (c) 0.2, (d) 0.3, (e) 1.0, (f) 2.0, and (g) 3.3 L. The PID spectra were taken with a photon intensity of  $33 \text{ mW/cm}^2$  at  $320 \pm 60 \text{ nm}$  and normalized to the respective TPD peak area shown in Figure 2 before photon irradiation.

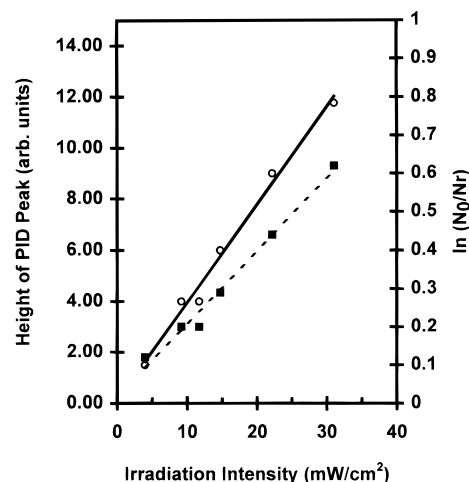
OCS molecule to dissociate/desorb under UV irradiation. Our results strongly suggest that the OCS molecule adsorbed on GaAs(100) has a higher photodesorption/photodissociation probability at lower initial coverages. However, the  $m/e = 28$  signal monitored in our PIDS experiment can be contributed from either the desorbing CO, a photodissociation product of adsorbed OCS, or the fragmentation of photodesorbed OCS in the mass spectrometer.

In our PIDS studies, we also monitored and observed the  $m/e = 60$  (OCS) MS signal right after removing the shutter, which indicated the existence of photodesorption of molecular OCS. To further confirm the photoinduced dissociation of adsorbed OCS, we carefully measured the ratio of  $m/e = 28$  and 32 signals during the photoradiation and compared it with that obtained in the thermal desorption of molecular OCS. If photoinduced dissociation of adsorbed OCS does occur, CO (product of photodissociation) together with OCS (photodesorption) would enter the mass spectrometer to cause an enhanced  $m/e = 28$  MS signal, leading to a higher ratio between  $m/e = 28$  and 32 MS signals than that obtained in TDS of molecular OCS. Indeed, the ratio obtained in PIDS is about 12 times higher than that due to the fragmentation of molecular OCS in the mass spectrometer. Therefore, we can conclude that both the photodesorption and photodissociation of OCS adsorbed on GaAs(100) occur concurrently at  $320 \pm 60 \text{ nm}$ .

To investigate the effect of irradiation time on the photochemistry of adsorbed OCS molecules, we dosed 1.0 L OCS onto the surface at 100 K, followed by irradiation of UV light ( $11 \text{ mW/cm}^2$ ,  $320 \pm 60 \text{ nm}$ ). The remaining OCS on the surface after irradiation, measured by TPD, is plotted as a function of irradiation time, shown in Figure 4. An exponential decay can be seen from the figure, indicating a first-order process to the OCS coverage. The effect of light intensity was also studied by fixing the irradiation time to 25 s and varying the light intensity. The logarithm of the ratio of remaining and initial OCS, together with the intensity of the PIDS peak representing the initial rate of the photoreaction, was calculated and plotted against light intensity (Figure 5). Both  $\ln(N_0/N_t)$  and PIDS peak intensity show linear relationships with the light intensity, which



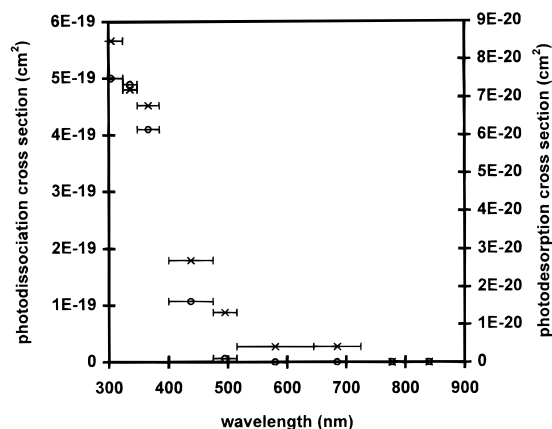
**Figure 4.** Plot of the amount of OCS ( $m/e = 32$ ) remaining on the surface vs irradiation time. The surface was exposed to 1.0 L OCS at 100 K and then irradiated with the light at  $11 \text{ mW/cm}^2$  and  $320 \pm 60 \text{ nm}$ . Postirradiation TPD spectra were obtained with a heating rate of 5 K/s.



**Figure 5.** Photoreaction of OCS (1.0 L) on GaAs(100) at 100 K, studied by varying the photon intensity at  $320 \pm 60 \text{ nm}$ . An irradiation time of 25 s was kept constant. TPD spectra ( $m/e = 32$ ) for the OCS remaining on the surface after irradiation were measured at a heating rate of 5 K/s.  $N_0$  stands for TPD peak area of OCS without irradiation while  $N_t$  for that after irradiation. The peak heights in PID spectra ( $m/e = 28$ ) taken during the irradiation process are also presented here: (■)  $\ln(N_0/N_t)$ , (○) height of the PID peak.

demonstrates a single-photon process involved in the photochemical reactions. A total cross section of about  $4.7 \times 10^{-19} \text{ cm}^2$  for photodesorption and photodissociation can be calculated from the gradient of the  $\ln(N_0/N_t)$  vs light intensity curve.

Wavelength dependence of the cross section was measured using a variety of long pass filters ranging from 285 to 850 nm. These filters cut the spectrum of the xenon lamp into a few sections. The infrared ( $\lambda > 900 \text{ nm}$ ) part of the lamp spectrum was removed by a water filter. When a long pass filter was used, the light with  $\lambda > \lambda_{\text{cut-on}}$  could transmit through and irradiate the surface. Thus, the  $\ln(N_0/N_t)$  obtained using a particular filter is actually  $\sum_i \sigma_i f_i$  ( $N_0$  and  $N_t$  are the adsorbed OCS before and after irradiation, respectively;  $\sigma_i$  is the cross section for light in  $i$ th section with an intensity of  $f_i$ ). The summation includes all those sections with  $\lambda > \lambda_{\text{cut-on}}$ . The difference between the two summations, obtained using two adjacent filters, gives  $\sigma_i f_i$ . Thus  $\sigma_i$ , the cross section in the  $i$ th section, can be readily calculated. However, the cross section obtained based on  $\ln(N_0/N_t)$  is the total cross section for photodesorption and photodissociation. The contribution of photodesorption should be isolated from the total cross section to obtain the photodissociation cross section. This was realized by integrating the desorption area of OCS in its PID spectrum of  $m/e = 60$  measured during irradiation. Figure 6 shows the



**Figure 6.** Wavelength dependence of the cross section for photoinduced dissociation and desorption of OCS on GaAs(100) with 1.0 L OCS initially dosed at 100 K: (○) photodissociation cross section, (×) photodesorption cross section.

photodissociation and photodesorption cross sections as a function of wavelength. In general, we observed that OCS adsorbed on GaAs(100) dissociates upon irradiation in the near-UV range with a cross section of the order of  $10^{-19}$  cm<sup>2</sup> which decreases as wavelength increases. The cross section for photodissociation becomes undetectable above 480 nm. In contrast, the photodesorption cross section ( $\sim 10^{-20}$  cm<sup>2</sup>) is 10-fold lower than that for photodissociation. It is also interesting to note that photodesorption has a threshold photon energy ( $\sim 770$  nm) much lower than that ( $\sim 480$  nm) for photodissociation.

## Discussion

OCS adsorbs molecularly on GaAs(100) at 100 K. By assuming a first-order desorption and a pre-exponential factor of  $10^{-13}$ , we obtained a desorption energy of 39 kJ/mol,<sup>22</sup> indicating a weak interaction between OCS and GaAs(100). This result also implies that the ground state of adsorbed OCS molecules is not significantly perturbed.

Our PIDS studies clearly indicate that at a lower coverage adsorbed OCS has a relatively higher probability to photodissociate/photodesorb from the surface. A factor of  $\sim 5.5$  enhancement was observed for 0.03 L OCS exposure compared to that for 3.3 L. Polanyi and co-workers studied the photochemistry of OCS adsorbed on LiF(001)<sup>17</sup> and observed that the OCS photodissociation cross section decreases from  $3.3 \times 10^{-16}$  to  $2 \times 10^{-17}$  cm<sup>2</sup> as the dosage is increased from  $2 \times 10^{-4}$  L to 0.11 L. In their work, the significant enhancement at low OCS coverage was attributed to the presence of surface defects. OCS molecules adsorbed on the defect sites are expected to be deformed, hence inducing a higher photodissociation cross section. Such an enhancement was obvious only at low coverage due to the limited amount of defects present on the surface. This mechanism was further confirmed by their observation of reduction in the extent of enhancement after annealing. In contrast, the enhancement observed in our experiment is not limited only to the low OCS coverages. In fact, we observed a gradual decrease in the photodissociation/photodesorption yield as increasing the OCS exposure up to saturation at 1 L (Figure 3). Above 1 L, the intensity of PID spectra is expected to be almost constant since the initial coverage of OCS reaches stagnation (Figure 2). Obviously, the possible contribution from surface defects at low coverages could not fully account for our results. The other possibility is that the local chemical environment of adsorbed OCS on GaAs(100) changes as the coverage is increased. The coupling

between the photogenerated carriers and adsorbed OCS may be strongly dependent on the local electronic structures near the adsorbed molecules. A detailed study of OCS adsorption is necessary in order to further confirm this mechanism.

The exponential decay of the remaining OCS with irradiation time (Figure 4) and the linear dependence of the initial photoreaction rate on light intensity (Figure 5) strongly suggest that the photochemical process of adsorbed OCS on GaAs(100) is first-order to the OCS coverage and involves a single photon. The thermal contribution caused by irradiation can be ruled out since the temperature rise observed during the irradiation is negligible. Furthermore, it was demonstrated that laser-induced thermal desorption shows a strongly superlinear dependence on fluency.<sup>21</sup> In our experiment,  $\ln(N_0/N_t)$  as well as the initial reaction rate measured by PIDS, varies linearly with light intensity, which clearly rules out the possibility of a thermal effect. The photochemical process of OCS on GaAs(100) can be described by  $N_t = N_0 \exp(-\alpha t)$  or  $(dN_t/dt)_{t=0} = \phi \sigma N_0$ .

The wavelength dependence of photodissociation cross section of OCS adsorbed on GaAs(100) shows that the dissociation mainly occurs in the UV range (Figure 6). In the gas phase, the OCS dissociation cross section is about  $10^{-21}$  cm<sup>2</sup> at 250 nm and reaches a maximum of  $\sim 1 \times 10^{-19}$  cm<sup>2</sup> at 222 nm.<sup>11</sup> Polanyi and his co-workers<sup>14</sup> observed that OCS on LiF(001) possesses a photodissociation cross section of  $10^{-16} \sim 10^{-17}$  cm<sup>2</sup> at 222 nm, which is 2–3 orders of magnitude higher than the gaseous value. This significant enhancement in photoreaction was attributed to the interaction of adsorbed OCS with photogenerated excited F centers in the substrate surface. Zhou and White reported a photodissociation cross section of  $\sim 4.4 \times 10^{-20}$  cm<sup>2</sup> for OCS on Ag(111) at 254 nm.<sup>12</sup> Two possible mechanisms were suggested to be involved in these photoreactions. In addition to the direct excitation of the OCS–Ag complex, the photoexcited substrate electron–hole pairs interact with the adsorbate, causing the desorption or dissociation. In some other cases, such as the photochemical studies of SO<sub>2</sub>/Ag(111),<sup>19</sup> O<sub>2</sub>/Pd(111),<sup>20</sup> and CCl<sub>4</sub>/Ag(111),<sup>23,32</sup> the photoelectrons generated during irradiation can attach to the adsorbate to form an anion which subsequently dissociates.

In our experiment, we observed that the photodissociation cross section has the order of  $10^{-19}$  cm<sup>2</sup> in the UV range of about 300 nm and becomes undetectable at about 480 nm. This cross section is significantly greater than that obtained on Ag(111) by Zhou and White. The photon energy ( $\lambda > 300$  nm) employed in this experiment is at least 0.8 eV lower than the absorption threshold ( $\lambda = 255$  nm) of OCS in the gas phase. Combining the above with the fact of weak interaction between OCS and GaAs(100), the direct absorption mechanism, in which adsorbed OCS is excited to a repulsive potential by absorbing a photon, may not play an important role. In addition, the electron affinity of GaAs(100) is about 4.1 eV (the lowest energy level of conduction band),<sup>24</sup> which is already about the high limit of the photon energy (2.6–4.1 eV), causing the photodissociation of adsorbed OCS observed in this experiment. Thus the photoelectron attachment is not likely to be the dominant process. In the present work, the interaction of photogenerated “hot” carriers in the substrate surface of GaAs(100) is considered to be the major channel accountable for the observed results. In this mechanism,<sup>12,25–31</sup> an electron in the valence band absorbing a photon is excited to the conduction band, forming an electron–hole pair. The pair penetrates to the surface and localizes on the adsorbate, with the electron of the pair penetrating into the antibonding orbital of the adsorbate and the hole being filled by the electron from the highest occupied bonding orbital of the adsorbate. Hence, energy is transferred

to the adsorbate to cause dissociation or desorption. Furthermore, the attachment of zero-energy photoelectrons created at 300 nm to adsorbed OCS is also a possible mechanism.

Zhou and White<sup>12</sup> observed a red shift of about 1.9 eV in threshold energy for photodissociation of OCS adsorbed on Ag(111), compared with that of gas phase OCS. This red shift was explained by a strong coupling of the excited states of the adsorbate–substrate complex with substrate conduction orbitals. Compared to the isolated excited adsorbates in the gas phase, this interaction is expected to stabilize the excited adsorbate–substrate complex and subsequently lower the potential energy of the excited state, causing a red shift in photodissociation. This mechanism can also be employed to explain the red shift of about 2.4 eV observed in our experiment.

To account for the enhancement of the photodissociation cross section for OCS adsorbed on GaAs(100), the photogenerated electron–hole pair penetrates to the OCS–Ga complex at the surface, the electron of the pair localizes on the OCS by taking the  $4\pi^*$ -derived orbital, while the  $3\pi$  orbital electron in the OCS recombines with the hole. If we assume the localized electron has zero momentum, then in the whole process momentum is conserved and the participation of phonons is not required. Such a process is expected to have a higher probability than the photoelectron attachment in which a phonon has to be involved to keep momentum conservation. The substrate used in our experiment is a chip of intrinsic GaAs semiconductor. There are few free electrons in the conduction band. The holes in photoexcited electron–hole pairs are not likely to be neutralized by free electrons in the conduction band. Therefore, the electron–hole pairs have relatively longer lifetimes to migrate to the surface. In addition, GaAs is a direct band gap semiconductor in which electron–hole pairs can be excited by photons more readily. The quenching of the excited adsorbate–substrate complex may be much faster on Ag(111) than that on a semiconductor surface such as GaAs(100). All these can account for the fact that OCS on GaAs(100) has a higher photodissociation cross section of  $\sim 4.7 \times 10^{-19} \text{ cm}^2$  at 300 nm than that of  $\sim 4.4 \times 10^{-20} \text{ cm}^2$  on Ag(111) at 254 nm observed by Zhou and White.<sup>12</sup> A detailed comparison between this and the previous study on the photochemistry of OCS on LiF(100)<sup>14</sup> was not attempted due to the large difference in the photon energies employed.

The photodesorption observed is also attributable to the photogenerated carriers. The excited OCS–substrate complex formed through the interaction with carriers can be quenched back to the ground state with excited vibration motions, leading to desorption. In fact, the threshold energy for photodesorption of OCS adsorbed on GaAs(100) is about 1.6 eV, near the band gap of the semiconductor substrate (1.42 eV).<sup>24</sup> The difference in the threshold energies for photodissociation (2.6 eV) and photodesorption (1.6 eV) is probably due to the energetic difference between the final states involved in these two processes.

## Conclusion

OCS adsorbs molecularly onto GaAs(100) at 100 K. Adsorbed OCS molecules either dissociate into gaseous CO and adsorbed S or desorb as gaseous molecular OCS upon UV irradiation. Our results clearly show that the photochemical

process involves a single photon and is first-order to the coverage of OCS. At lower coverages, adsorbed OCS molecule has a relatively higher probability to photodesorb/photodissociate. The photodissociation cross section is on the order of  $10^{-19} \text{ cm}^2$  for UV light at about 300 nm. It decreases rapidly as the wavelength increases and becomes undetectable at 480 nm. The cross section for photodissociation of OCS on GaAs(100) at 300 nm is about  $10^2$  higher than that for gaseous OCS at 250 nm and about 10-fold greater compared with OCS on Ag(111) at 254 nm. The photodissociation and photodesorption are found to have threshold energies at 2.6 and 1.6 eV, respectively.

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