

A mechanistic study of CO₂ reduction at the interface of a gallium phosphide (GaP)
surface using core-level spectroscopy

Kristen Flynn

Mentor: Dennis Nordlund

Co-advisors: Dimosthenis Sokaras, Craig Schwartz, Hirohito Ogasawara, and Tsu-Chien
Weng

Stanford Synchrotron Radiation Light Source, Stanford, CA
Science Undergraduate Laboratory Internship, Summer 2015
August 14, 2015

SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025

*This material is based upon work supported by the U.S. Department of Energy, Office of Science,
Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate
Laboratory Internship (SULI) program, under Contract No. DE-AC02-76SF00515.*

Abstract

Carbon dioxide (CO₂) emission into the atmosphere has increased tremendously through burning of fossil fuels, forestry, etc.. The increased concentration has made CO₂ reductions very attractive though the reaction is considered uphill. Utilizing the sun as a potential energy source, CO₂ has the possibility to undergo six electron and four proton transfers to produce methanol, a useable resource. This reaction has been shown to occur selectively in an aqueous pyridinium solution with a gallium phosphide (GaP) electrode. Though this reaction has a high faradaic efficiency, it was unclear as to what role the GaP surface played during the reaction. In this work, we aim to address the fundamental role of GaP during the catalytic conversion, by investigating the interaction between a clean GaP surface with the reactants, products, and intermediates of this reaction using X-ray photoelectron spectroscopy. We have determined a procedure to prepare atomically clean GaP and our initial CO₂ adsorption studies have shown that there is evidence of chemisorption and reaction to form carbonate on the clean surface at LN2 temperatures (80K), in contrast to previous theoretical calculations. These findings will enable future studies on CO₂ catalysis.

Introduction:

The increase in concentration of greenhouse gases (i.e. – carbon dioxide (CO₂)) over recent years has made global warming an evident issue as world temperature raises, climate changes, etc. The greenhouse effect states some atmospheric gases allow the transmittance of the sun's radiation (shorter wavelength) and the reflection of infrared radiation (longer wavelength) off the earth's surface maintaining the earth's temperature.¹ Emissions of these atmospheric gases (i.e. – CO₂, methane, etc.) increase the greenhouse effect due to their ability to trap heat before it escapes into space.²

As noted, CO₂ production can be quite impactful on the environment though it is inevitable unless the energy system based on fossil fuel is reformed. It has been postulated that excess CO₂ can be utilized as a carbon source to synthesize longer hydrocarbon chains with greater value. CO₂ reactions have been heavily investigated recently as means to counteract the severe effects of global warming.

Although the reduction of CO₂ seems very promising in developing a route to decrease the concentration in the atmosphere, the reaction itself however is uphill and requires an input energy source.³ Since the sun can power most of the earth's energy needs, the use of sunlight as a potential energy source to convert CO₂ will aid in developing a sustainable energy landscape. These include novel electro- or photocatalysis processes to produce hydrogen and convert emitted CO₂ into fuels.

In recent literature, the electro-catalytic reduction of CO₂ to several products such as formic acid, methanol (CH₃OH), carbon monoxide, etc. have been studied. Through the usage of different electrodes, faradaic efficiency (electron charge conversion) of up to 100% has been noted in several aqueous reactions.⁴⁻⁷

Unfortunately, electrochemistry in aqueous solutions does not always yield pure product, but rather a mixture. Separation of both the anode and cathode in two different solutions is vital because it stops the reversion of products to reactants, specifically if the reactants have lower ground state confirmation energy. It is also important to note that protons are flowing from a source within the aqueous solution concurrently with the electrons throughout the reaction.

A study done by Cole, *et. al.*, showed that one can reduce CO₂ to CH₃OH using an aqueous solution of pyridinium (proton source). It was postulated that the mechanism

proceeds via a six-electron transfer solely utilizing pyridinium as both the electron and proton transfer molecule.⁸ Further mechanistic studies of the overall role of pyridinium were done by Cole, *et. al*, alluding to the potential selectivity one can achieve by varying the substituents on the aromatic ring.⁹

However, their findings suggested that formic acid was inevitable regardless of substitution, ranging from trace amounts to 12% faradaic efficiency.¹⁰ Formic acid isn't very beneficial, as it must be further derivatized to be useful. The utilization of surface chemistry has exhibited promising results to selectively convert to CH₃OH only. This conversion has been shown to occur selectively in an aqueous pyridinium solution with a gallium phosphide (GaP) electrode and approaches faradaic efficiency values up 100% solely using light energy.¹¹

In this study, we aimed to investigate the role of atomically clean GaP(111) during the reaction by studying the chemical bonding between the surface and the active species using core-level spectroscopy. Utilizing x-ray photoelectron and x-ray absorption spectroscopy to probe the local electronic structure and changes upon absorption in both the surface and absorbent, we have developed a route to prepare atomically clean GaP. We have also shown that CO₂ appears to chemisorb on the surface at LN2 temperatures, which seems at odds with the energetics of CO₂ adsorption on GaP surfaces predicted theoretically.¹²

Methods:

A p-type GaP(111) wafer was purchased and analyzed as is from the distributor (MTI Corporation) using core-level spectroscopy to determine the contamination present. XPS was utilized to determine the chemical nature of the atoms present in the sample whereas XAS was used to probe the local unoccupied electronic structure.¹³⁻¹⁴ Under (UHV) high vacuum conditions, the wafer was sputtered with argon at 2 mA/cm² for 30 mins and then annealed to 350°C for 30 mins. The wafer was then exposed to CO₂ twice at LN2 temperature (80K) to ensure adsorption.

XPS and XAS data was collected at beamline 10-1 at Stanford Synchrotron Radiation Lightsource (SSRL). The wiggler beamline has a spherical grating monochromator that covers the energy range from 200 to 1200 eV. Energy calibration

was done to residual carbon 1s signal found in the sample which was set to a binding energy of 284.8 eV. Background subtraction was done using preinstalled background functions in PyMca version 5.0.1.¹⁵

Results and Discussion:

Core-level spectroscopy was used to investigate the state of the GaP(111) surface before surface cleaning, after surface cleaning and upon adsorption of CO₂. After assessment of the XPS overview for GaP(111) and a gold reference before cleaning, we found that there was some oxide and surface contamination on the surface. An atomically clean surface would have two peaks present corresponding to gallium 3d at 19 ± 1 eV and phosphorus 2p at 130 ± 1 eV. Though these two peaks are present in GaP(111) in Figure 1, there is also a notable carbon 1s peak at 286 eV and a oxygen 1s peak at 532 eV. However, the gold reference has oxygen and carbon contamination present at the same binding energies indicating that there is an energy shift present. In the following, the energy scale scale has been shifted such that the residual carbon is at 284.8eV.

In Figure 2, we show high resolution XPS measurements (~ 0.4 eV total energy resolution) excited at 650eV. Atomically clean GaP(111) surface was prepared by sputtering and annealing several times under UHV. After just sputtering for 30 mins, there was notable increase in both the gallium and phosphorus peak (Figure 2, top row). It should be noted that although the oxygen peak increased after just sputtering, XPS at our excitation energy is very sensitive in identifying trace amounts of oxygen (The mean free path for O1s photoelectrons at $(650-530)=120$ eV kinetic energy is less than 10 angstrom and the subshell ionization cross-section is very high. We also note that there might be some increased residual oxygen due to increased surface area after sputtering). A more accurate representation of the oxygen chemically bonded to gallium (Ga) and phosphorus (P) near the surface is is the band to the right of the phosphorus 2p transition at 134 ± 2 eV (Figure 2, top right), which is chemically shifted relative to the (semi) metallic P. It's evident that after sputtering, the oxidized P peak decreases showing that oxygen was partially eliminated from the surface. Sputtering in conjunction with annealing showed promising results, as the ratio of gallium to carbon was reduced to 8:1

and phosphorus to carbon to 6:1 (compared to X:Y and X:Y for the as-is sample before cleaning).

As the carbon peak begins to subside and broaden out, there is an apparent increase in the sidebands of the carbon 1s (Figure 2, bottom left). This band corresponds to a different type of carbon present, which hasn't been accounted for yet, but it is consistent with a small fraction of atomic carbon in the GaP substrate. In turn, this introduces a degree of error for the standard energy calibration of carbon set to 284.8eV, which we have kept to be consistent with literature.¹⁷ Correction for this error can be accounted for by determining the Fermi level and/or the work function for the GaP surface, which is outside the scope of this report.

Due to time constraints, complete atomically clean GaP was not achieved in time for initial CO₂ adsorption studies. but the fraction of oxygen and carbon relative to the Ga and P signals was deemed sufficiently low for preliminary studies of the CO₂ adsorption. Figure 3 shows the XPS before and after 2 exposures of the near clean GaP surface to CO₂ at LN₂ temperature at the same excitation energy. In the carbon 1s, we note that the total intensity near 293 ± 1 eV increases after both exposures, but that there is no significant peak around 291eV where we would expect physisorbed CO₂ to occur.¹⁸ The higher energy peak can be associated with carbonate formation, CO₃. Concurrently, we notice a shoulder near 534eV in the oxygen region, which is also consistent with carbonate functionalities. .

Thus, we have proposed that CO₂ would chemically interact with GaP, with a small oxygen coverage, forming carbonate functionalities. The minimal dissociation shown in the preliminary studies suggest that GaP(111) is catalytically active during the reaction as CO₂ is reduced. Future studies with pure GaP(111) will provide a better mechanistic understanding of how the surface interacts with pyridinium and other active species that occur during the reaction.

Conclusion:

We have demonstrated that atomically clean GaP(111) can be achieved through reiteration of sputtering and annealing. We have also shown that CO₂ does in fact chemisorb in the presence of GaP(111) at two different exposure pressure. Specifically

1.03E-5 torr was determined to be very promising although future studies will involve exposing the surface for a longer period of time following by XPS and XAS monitoring. Lastly, the Fermi level and the work function of GaP should also be determined to accurately perform an energy calibration on the data collected. Overall, the GaP(111) surface has shown promising results for CO₂ reduction.

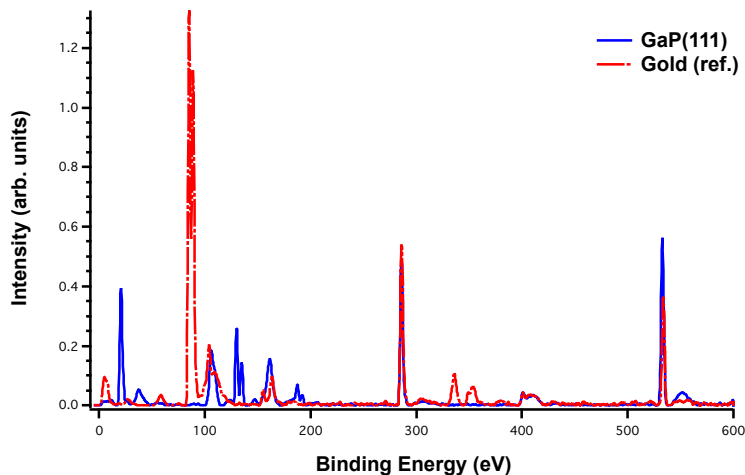


Figure 1. XPS overview of GaP(111) and a gold reference of surfaces as is.

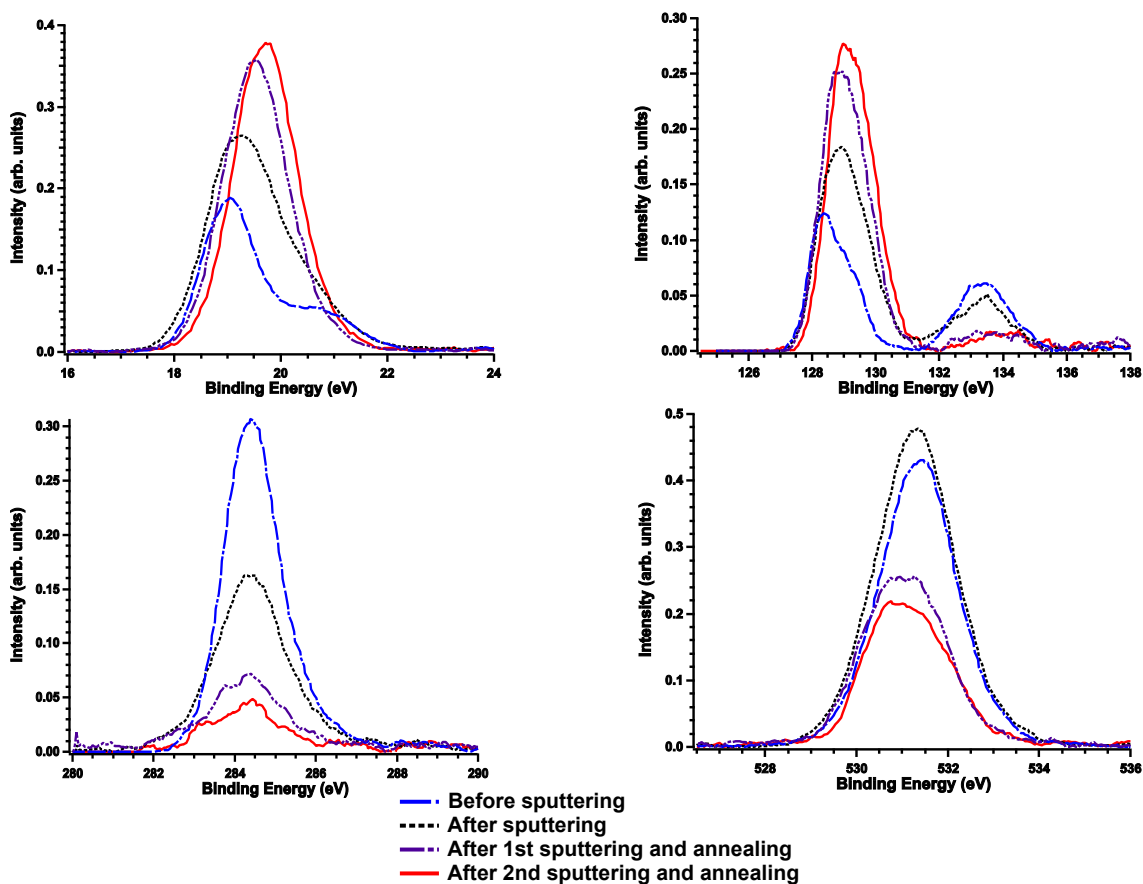


Figure 2. XPS spectrum collected during sputtering and annealing for gallium, phosphorus, carbon, and oxygen (right to left).

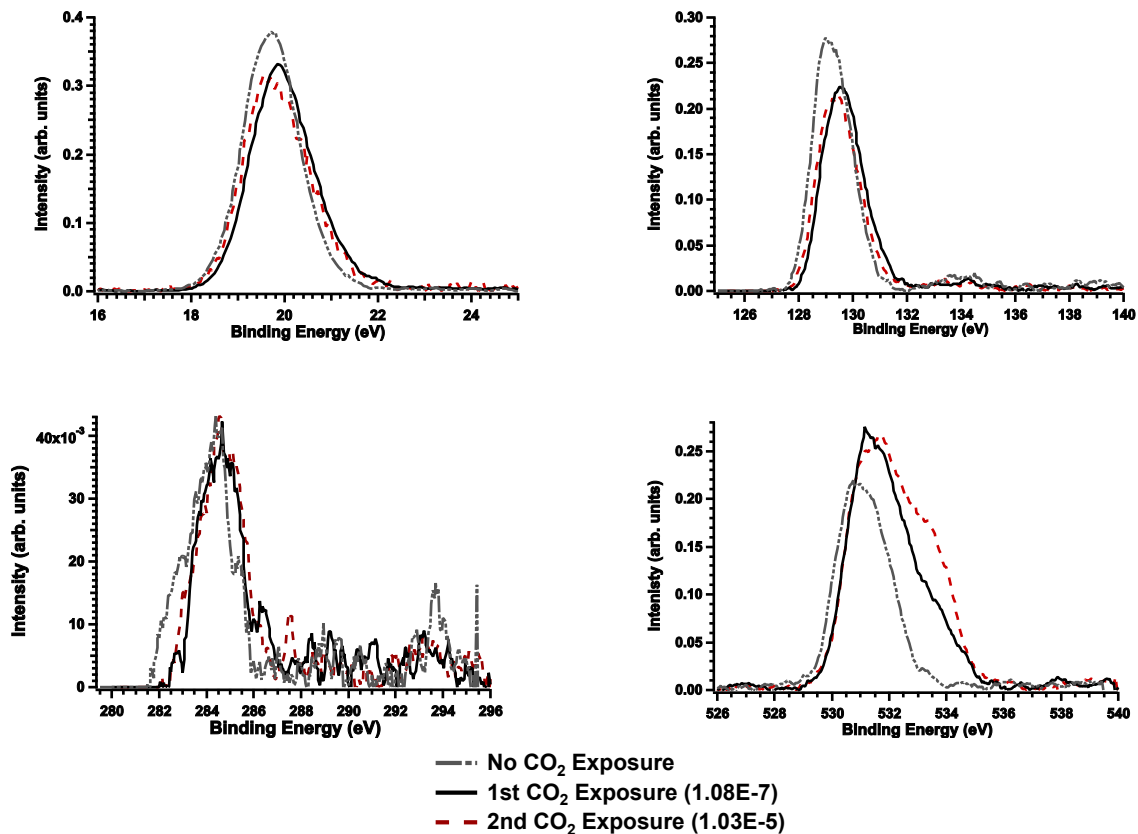


Figure 3. XPS data for exposure of the GaP(111) surface to CO₂ at two different leak in pressures, each 100 seconds long. The peaks correspond to gallium, phosphorus, carbon, and oxygen (from left to right).

Acknowledgements:

The author would like to acknowledge D. Nordlund, T. S. Weng, D. Sokaras, H. Ogasawara and C. P. Schwartz for the valuable discussions and continual help. The Office of Science, a branch of the U.S. Department of Energy, supported this research through the Science Undergraduate Laboratory Internship.

References:

1. D. G. Kessel, *J. of Petroleum Science and Engineering* **26**, (2000).
2. D. G. Kessel, *J. of Petroleum Science and Engineering* **26**, (2000).
3. E. B. Cole and A. B. Bocarsly, *Carbon Dioxide as Chemical Feedstock* (Academic, Germany, 2010), Chapter 11, p. 291.
4. A. Coehn and S. Jahn, *Chem. Ber.* **37** (1904)
5. J. Ryu, T. N. Andersen, and H. Eyring *J. Phys. Chem.* **76**, (1972).
6. D. Summers, S. Leach, and K. Frese, *J. Electroanal. Chem.* **189**, (1986).
7. E. B. Cole and A. B. Bocarsly, *Carbon Dioxide as Chemical Feedstock* (Academic, Germany, 2010), Chapter 11, p. 300-302.
8. E. B. Cole, P. S. Lakkaraju, et. al. *J. Am. Chem. Soc.* **132**, (2010).
9. E. E. Barton Cole, M. F. Baruch, et. al. *Top. Catal.* **58**, (2015).
10. E. E. Barton Cole, M. F. Baruch, et. al. *Top. Catal.* **58**, (2015).
11. E. E. Barton, D. M. Rampulla, and A. B. Bocarsly, *J. Am. Chem. Soc.* **130**, (2008).
12. J. A. Keith, A. B. Muñoz-García, et. al. *Top. Catal.* **58**, (2015).
13. N. Mårtensson and A. Nilsson, *Application of Synchrotron Radiation; High Resolution Studies of Molecules and Molecular Adsorbates*, edited by W. Eberhardt (Springer, Berlin, Heidelberg, 1995), Vol. **35**.
14. J. Stöhr, *NEXAFS Spectroscopy* (Springer-Verlag, Berlin, Heidelberg, 1992).
15. V.A. Solé, E. Papillon, et. al. *Spectrochim. Acta Part B* **62** (2007).
16. NIST X-ray Photoelectron Spectroscopy Database, Version 4.1 (National Institute of Standards and Technology, Gaithersburg, 2012).
17. NIST XPS Data Field Definitions: Description of Data Field, Version 4.1 (National Institute of Standards and Technology, Gaithersburg, 2012).
18. H.-J. Freund and M. W. Roberts, *Surface Science Reports* **25**, (1996).