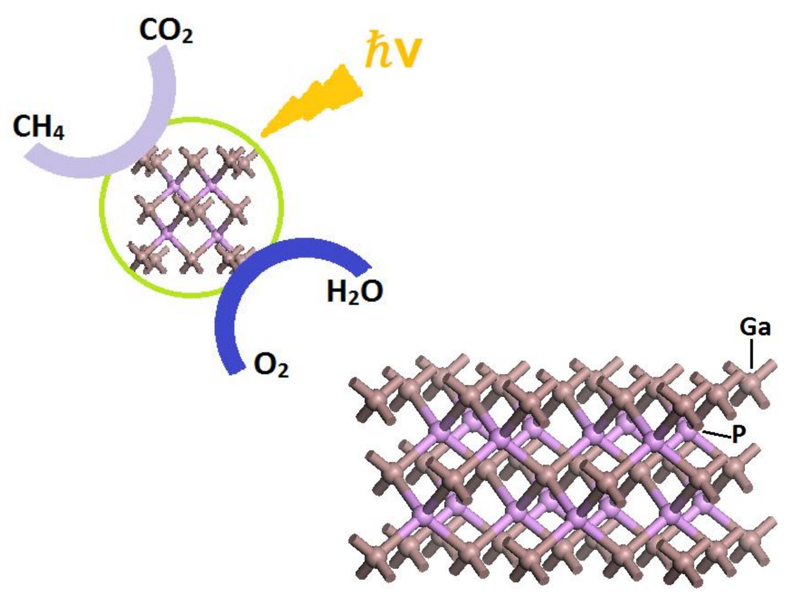
Study on the Transport Properties of GaP and p-type GaP Enhancement for the Reduction of CO_2 to Methane

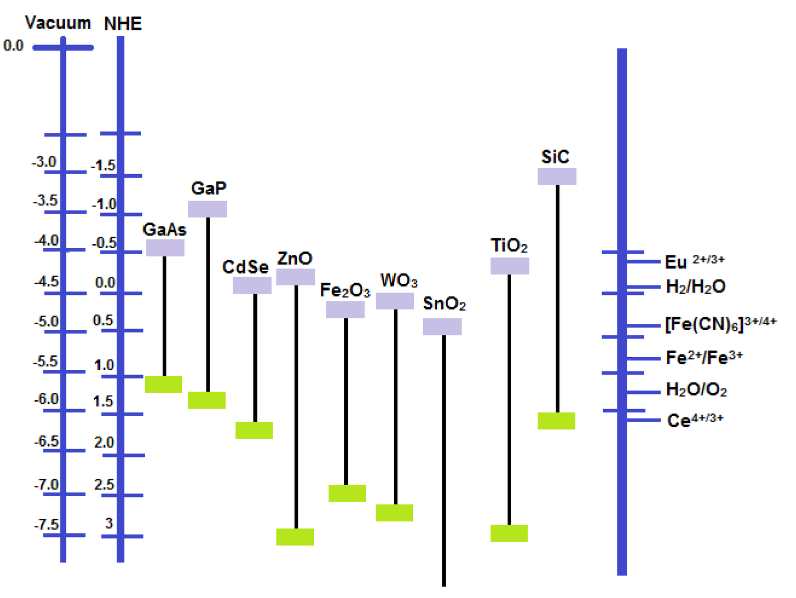
Shermin Arab[1], Stephen Cronin[1]

[1]Department of Electrical Engineering, University of Southern California, Los Angeles

Artificial Photosynthesis

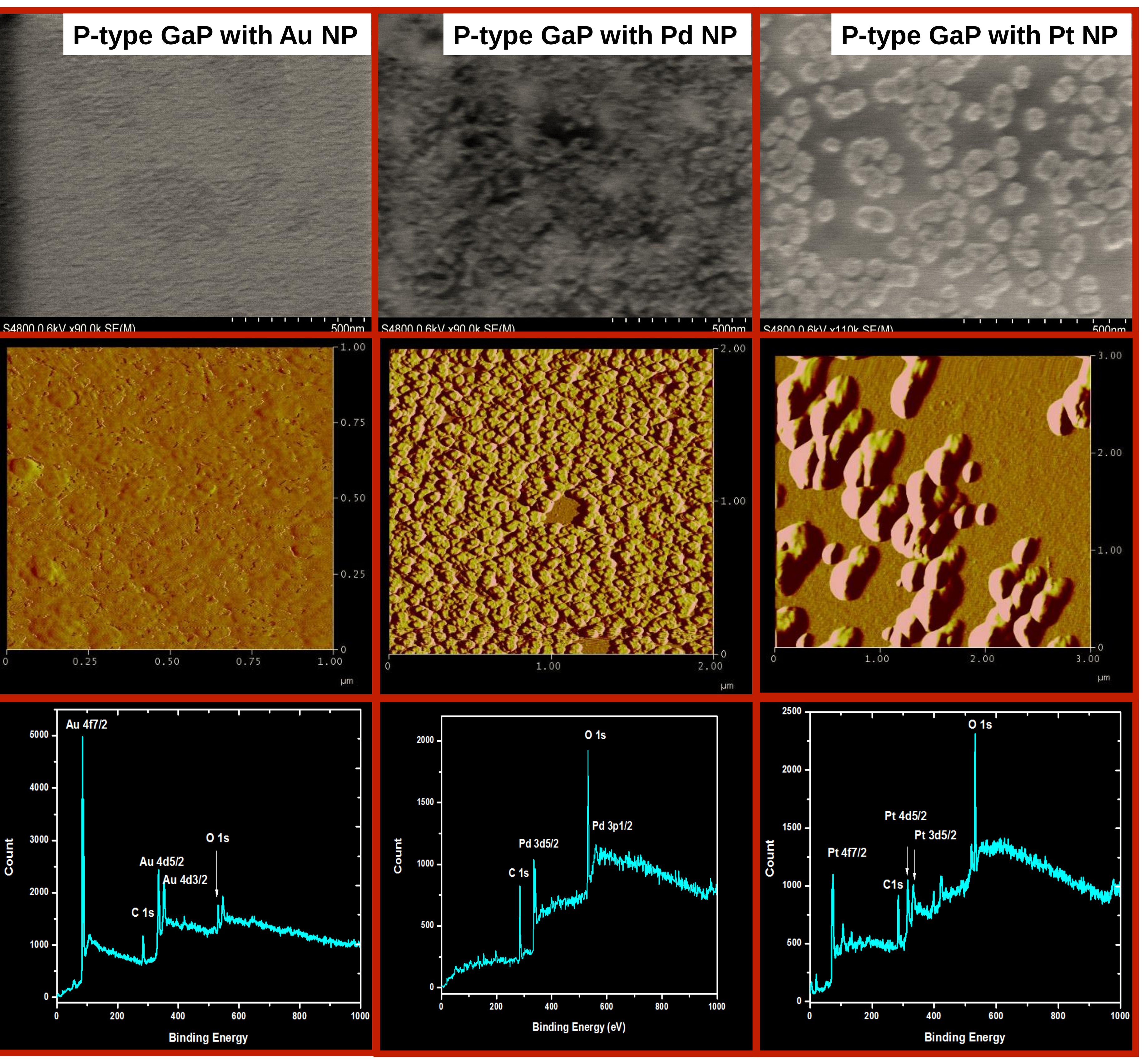


Chemical CO_2 mitigation [1] is referred to the process of atmospheric CO_2 reduction to other practical hydrocarbons without the production of excess CO_2. The reduction process of CO_2 to methane at the p-type semiconductors has been investigated by different research groups. Nevertheless, performance of this reaction under no applied voltage but radiated visible light is the matter of interest and its feasibility is still under study.



GaP as a small band gap semiconductor, has several outstanding optoelectric properties which make it suitable for several energy harvesting applications including H_2-generation through water splitting and CO_2 reduction to functional hydrocarbons. GaP has appropriate energy band edges in respect to CO_2 electropotential, with a conduction band which is about 1 eV more negative than the CO_2 reduction potential. The small band gap of GaP (2.27 eV equivalent to 546nm wavelength) is suitable for visible light absorption.

Composition and Structure



In order to have gas-phase reduction process we need to introduce a co-catalyst to the system This has been done by chemical deposition of Pd, Pt or Au nanoparticles (NP) on the surface of the p-type GaP. Above SEM and AFM images show the morphology of the NP on the GaP surface . XPS results confirm the existence of NP on the surface.

References

[1] A.B. Bocarsly et al., "Selective Solar-Driven Reduction of CO_2 to Methanol Using a Catalyzed p-GaP Based Photoelectrochemical Cell", JACS, 130, pp 6342-6344, 2007.

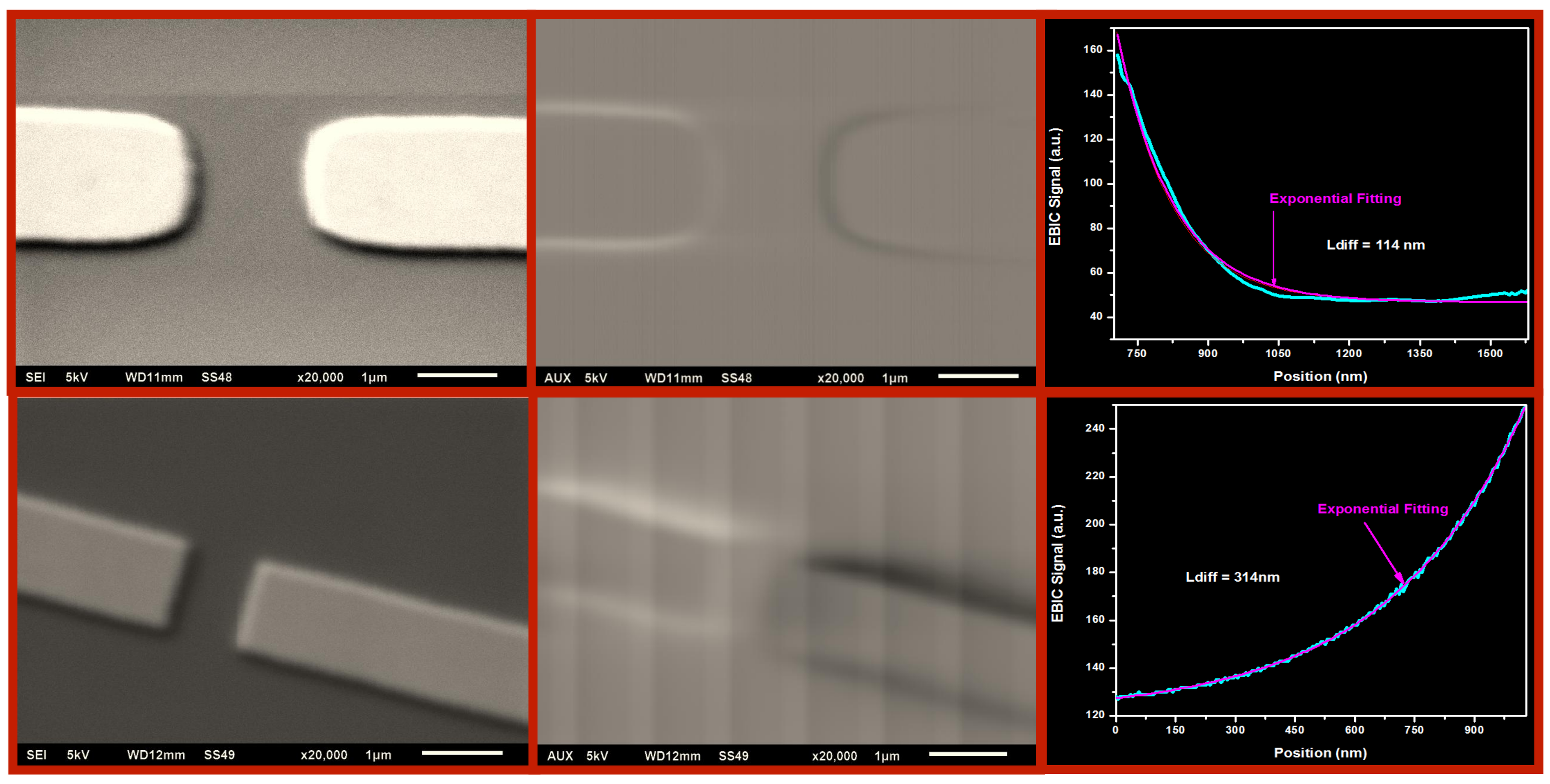
[2] S.A. Maier, "Plasmonics Fundamentals and Applications ", Springer, 2007.

Acknowledgements

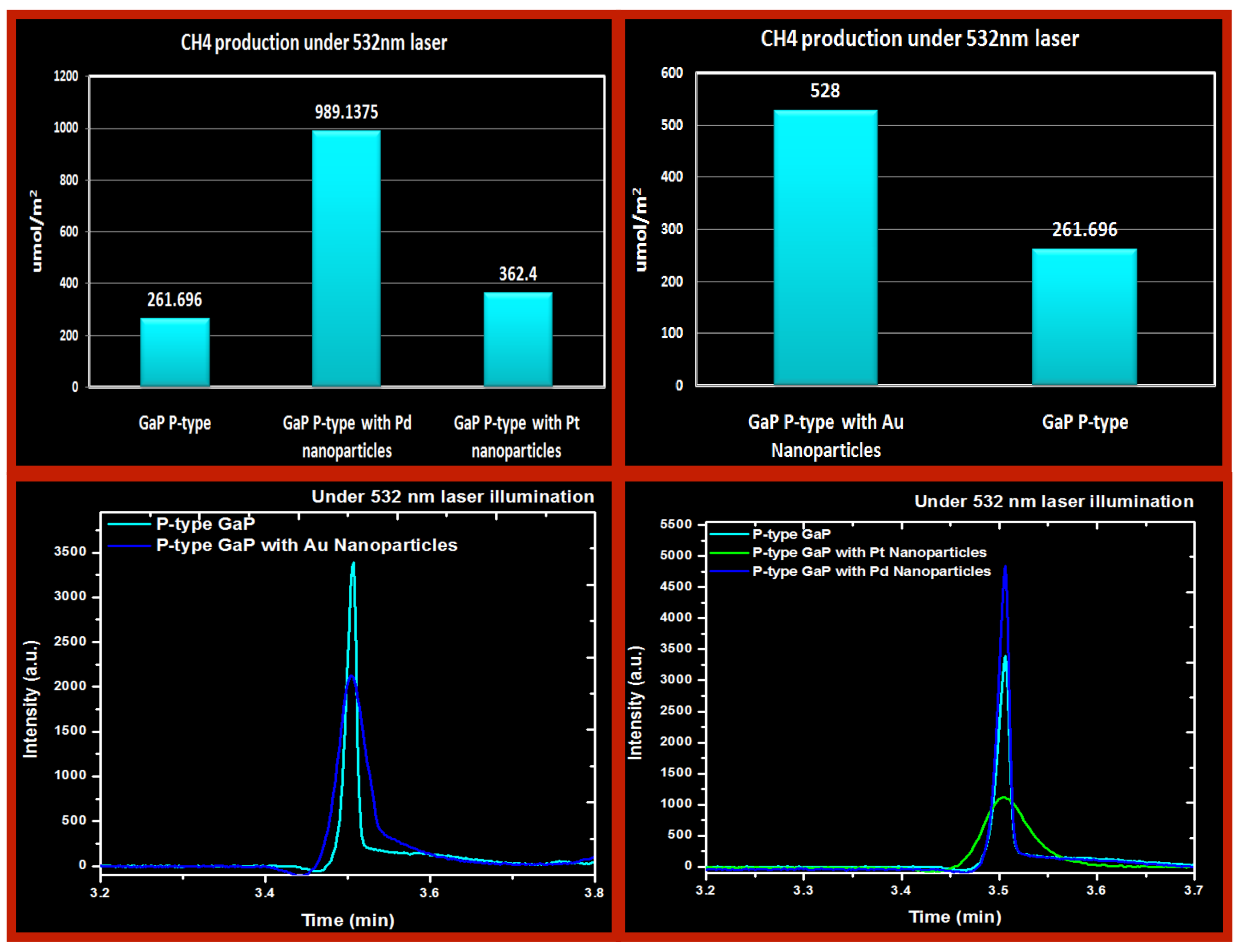
The authors gratefully acknowledge Prof. Brunschwig and the Molecular Material Research center at Caltech for XPS measurements and Prof. Narayan and Dr. Malkhandi for Nanoparticle deposition.

Electron Beam Induced Current Measurement (EBIC)

EBIC measurement is a method to study minority carrier diffusion length (carried in JEOL JSM-6610 SEM). In this method, electron–hole pair are created using focused electron beam within one minority carrier diffusion length of the metal semiconductor Schottky junction and on average creates a measurable current. Our results suggests L_{diff}= 112 nm for p-type GaP and L_{diff}=315 nm for n-type GaP.



P-type GaP a Photocatalyst for CO_2 Reduction to Methane



The photocatalysis reduction of CO_2 is studied using a stainless steel reactor with quartz window. A 532 nm laser has been used as the light source. Before the reactions starts, CO_2 is bubbled through deionized and flow through the chamber for 1 hour. Then the chamber is sealed and kept under irradiation at 70 C for 2 hours. The gas phase products are then analyzed using a Gas Chromatograph system (GC). The results of this experiment in the presence of three different configurations of P-GaP are demonstrated above. It is shown that presence of co-catalysts can increase the amount of produced methane. Pd and Au NPs have a significant influence which may be due to the CO production selectivity at these centers. The plasmonic enhancement effects of Au NP are also expected [2]; however, it is hard to distinguish the plasmonic induced improvement from co-catalyst effect .

Discussion & Future Work

Further enhancement in CO_2 reduction can be obtained by introduction of two co-catalysts at the same time but with different selectivity. We propose deposition of Pd nanoparticles(NP) and Au NP. In this case, Pd NP behave as H_2 production centers and Au NP behave as CO productions centers which together increases the formation of CH_4. On the other side, Introduction of Au leads to plasmon induced reactions and general enhancement in throughput. FTIR in situ measurement of the produced CH_4 and other hydrocatbons is another proposed methodology which we will use. In this method, we use a gas cell to continuously study the FTIR spectrum of the gases inside of the cell as the reaction occurs.

USC University of Southern California

USC Viterbi School of Engineering

Ming Hsieh Department of Electrical Engineering

Ming Hsieh Institute
Ming Hsieh Department of Electrical Engineering