



Femtosecond Soft X-Ray Probing of Electron Dynamics at Photocatalytic Material Surfaces

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REGENTS OF THE UNIVERSITY OF CALIFORNIA

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14. ABSTRACT A strategy that has found much success for semiconductor photocatalysis involves the creation of junctions of semiconductors with metals, either as thin films or as particles. Such materials are often observed to possess significantly higher activities and corrosion resistances when compared to a semiconductor alone. Understanding the effect of metal deposition on photocatalysts requires an understanding of the electronic structure of the junction as well as the behavior of the electrons and holes generated by solar radiation. In this report, A new apparatus has been constructed that produces extreme ultraviolet ultrafast laser pulses, which can be used for time resolved photoemission. Static spectra reveal the growth modes of metals on semiconductors and time-resolved studies show photovoltage shifts that reveal the dynamics of electron or hole carriers moving from one layer into another. In several studies, zinc junctions on silicon [Si(100)], both films and nanoparticles, and a Zn/n-GaP(100) junction were studied using the ultrafast time-resolved extreme ultraviolet (XUV) photoemission technique. The approach to metal character was revealed versus the size of the particles. Schottky barrier principles were elucidated, including new results demonstrating that core level transitions can reveal the changes in electron temperature in the same way as changes in Fermi electron distributions do. Using XUV transient absorption to look through a junction, layerspecific time-resolved results are obtained for the hole transport across a Si-TiO₂-Ni photoanode junction. The results indicate that the XUV photoemission and transient absorption techniques are highly suitable for studying the carrier dynamics of a wide range of junctions.			
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Abstract

This program investigates the formation of junctions and their physical properties. Zinc junctions with silicon [Si(100)], both films and nanoparticles, and a Zn/n-GaP(100) junction were studied using an ultrafast time-resolved extreme ultraviolet (XUV) photoemission technique. Using XUV transient absorption to look through a junction, layer-specific time-resolved results are obtained for the hole transport across a Si-TiO₂-Ni photoanode junction. The results indicate that the XUV photoemission and transient absorption techniques are highly suitable for studying the carrier dynamics of a wide range of junctions.

Introduction

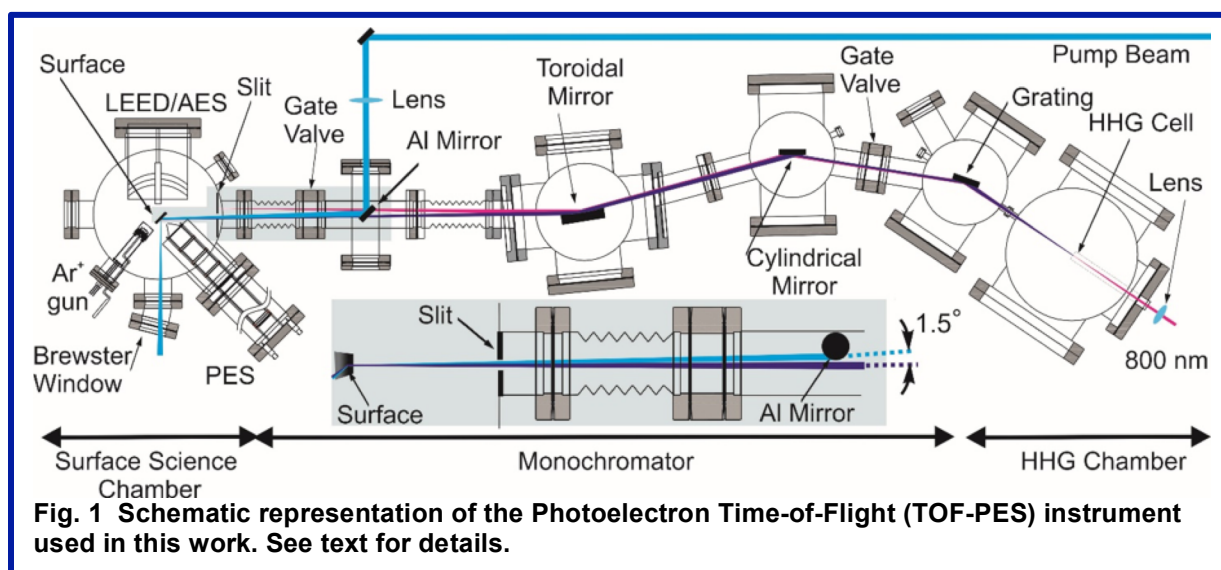
The overarching goal of this work is to obtain fundamental research knowledge that can improve the conversion of available sources of energy-rich materials such as biomass into useful fuels for the Air Force. The objectives are to investigate the charge-state dynamics at well-defined photocatalytic surfaces, interfaces, and junctions by means of extreme ultraviolet (XUV) ultrafast core-level electron photoemission and transient absorption spectroscopies. The time durations that charges remain at particular sites and how quickly they get there are basic measures of the effectiveness of charge separation and retention important for photocatalysis. Core level spectroscopies probe the transitions of electrons from inner shell orbitals to valence or conduction band states (transient absorption) or to the vacuum (photoemission). Core level spectroscopic methods are element-specific, charge- and oxidation-state sensitive, and even spin-state selective. The work in this final report investigated electron and hole charge state time dynamics, charge transfer, separation, and trapping at photocatalytic surfaces and interfaces. A new instrument uses high order harmonics of a Ti:sapphire laser in the XUV region of the spectrum to form ultrashort pulse durations (<50 fs) for photoemission. An ultrahigh vacuum surface science chamber allows cleaning and preparation of the sample surface, growth of materials, and characterization by static photoemission measurements and Auger spectroscopy during growth, to determine layer-by-layer growth. The photoemission method gives an inherently surface-sensitive view of the ultrafast dynamics within a few atomic layers of the catalytic surface. The XUV transient absorption method reports on the bulk materials and can

peer through junctions. The photocatalytic properties of materials, transport and charge separation of electrons and holes, and trap state effects are reflected in the ultrafast core-level photoemission/transient absorption measurements and depend on the semiconductor material, band alignment, metal or metal oxide co-catalyst, particle size and degree of oxidation.

1. Experimental

The new experimental setup consists of two main parts (i) the femtosecond (fs) laser system in conjunction with the pump-probe setup as well as the high order harmonics generation (HHG) system, and (ii) an ultra-high vacuum (UHV) surface science chamber. Figure 1 shows a schematic representation of the HHG setup together with the UHV chamber. Briefly, 800 nm pulses with pulse durations as short as 30 fs and with average powers up to 3 W at 1 kHz repetition rate are generated by an ultrafast oscillator and regenerative amplifier system. The output of this laser system is split into a pump arm and a probe arm. The 800 nm light in the probe arm is directed to the vacuum beamline, where it is focused to 10^{14} - 10^{15} Wcm⁻² into a semi-infinite gas cell (300 mm long) filled with rare gas atoms (typically argon). Through the high harmonic generation (HHG) process, photons with energies ranging from 15 eV to 100 eV can be created. After exiting the cell, the XUV and 800 nm radiation is dispersed by a plane grating to select a single harmonic order. The selected harmonic is focused using a cylindrical and toroidal mirror onto the sample surface, giving an XUV beam size of approximately 0.2 mm spatial extent. The discrimination of harmonics is further aided by a slit at the entrance of the chamber, which blocks unwanted harmonics from entering. For pump-probe experiments, the 800 nm light in the pump arm is directed to the sample by an aluminum mirror located slightly above the XUV beam path in the chamber directly before the surface science chamber. Through the use of BBO crystals the pump arm can be doubled or tripled to give 400 nm or 266 nm pump pulses for excitation of the semiconductor band gaps.

The UHV surface science chamber contains specific tools for surface preparation and characterization arranged on two levels. The upper level of the surface science chamber is



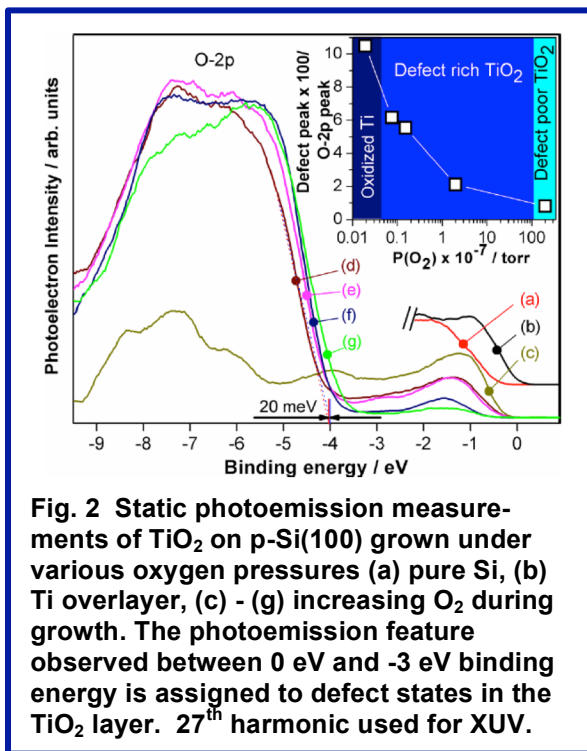
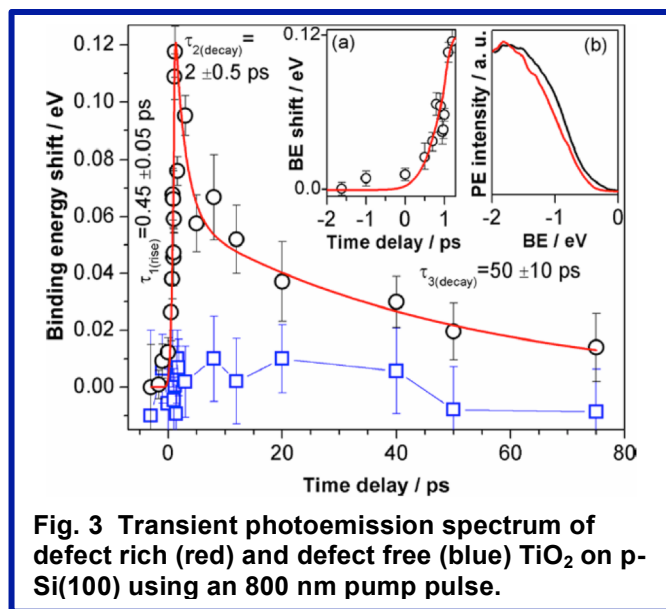
equipped with a homebuilt time-of-flight photoelectron spectrometer (PES) to investigate the electron dynamics at the surface of photocatalytic materials and an Ar ion gun for surface cleaning. The upper level of the surface science chamber is schematically represented in Figure 1. The lower level hosts an Auger electron spectrometer to investigate the surface composition and cleanliness, an ion gauge to measure the vacuum pressure, a gas inlet as well as a home built evaporator. The surface sample is attached to a liquid nitrogen cryostat and it is mounted in the center of the UHV chamber. The sample-cryostat assembly can be vertically translated to both vacuum chamber levels and horizontally rotated by 360° by a mechanical manipulator. Furthermore, an xy-horizontal translation stage allows a movement of the assembly by ± 12 mm from the midpoint. The sample position can be reproduced to better than 0.2 mm and 0.5° accuracy. The sample surface can be cooled down to 100 K and resistively heated up to 575 K. During the experiments a pressure of about 3×10^{-9} Torr is achieved in the surface science chamber by means of a multiple differential pumping stages. The obtained pressures are reduced from many Torr in the high HHG cell to ultrahigh vacuum in the surface science chamber.

The photoelectron spectra are measured by means of a home built TOF-PES. The 1 m long, double wall mu-metal tube of the TOF-PES houses 2 einzel lenses, which retard and collimate incoming electrons, and 2 stacked MCPs to detect and amplify signal from the measured electrons. Electron detection is accomplished by a microchannel-plate amplifier in

conjunction with a 5 GHz multichannel scaler electronics unit (FAST P7889) for data acquisition. Recent upgrades to the einzel lenses and multichannel scaler electronics unit have led to a 4 fold increase in overall photoelectron signal and resolution in the low kinetic energy regime. The sample surface is positioned 5 mm away from the PES entrance with the surface normal perpendicular to the spectrometer axis. The laser beam incidence angle is 45° . In order to avoid spectral shifting and broadening due to space charge effects, the pump beam intensity is carefully adjusted and the count rate is kept to at least half the value of the XUV count rate.

2.1 TiO₂/Si: Understanding defects in materials

Imperfections in semiconductor materials, such as atomic vacancies, interstitial atoms, or termination of the periodic lattice, result in the formation of electronic states that have energies within the bandgap of the semiconductor. These states influence the electronic properties of the semiconductor and can serve as recombination centers, thereby decreasing the carrier lifetime.



Thus, understanding how such states influence the electronic structure of materials is crucial to proper semiconductor design.

Characterization of defect states and their influence on charge transfer processes has been investigated in a semiconductor-semiconductor junction system of TiO₂ grown on p-Si(100), where the band alignment is strongly affected by defects. The relative band alignment of the defect free (defect poor) TiO₂/Si(100)

system is analyzed; upon irradiation with 800 nm light, electrons and holes that are generated in the Si substrate are not subsequently injected into TiO₂. In contrast, when the TiO₂ is produced with oxygen vacancies (defect rich), a change in the band alignment allows electrons to travel from the silicon to the TiO₂, while the photogenerated holes remain in p-Si(100), resulting in charge separation.

TiO₂ was grown with various oxygen vacancy defect concentrations by evaporation of Ti metal in different ambient O₂ pressures. Static photoemission measurements (shown in Fig. 2) were used to determine the electronic structure of the TiO₂ layer formed at O₂ growth pressures ranging from 7.5×10^{-9} Torr to 2.0×10^{-6} Torr. For the lowest O₂ pressures, photoemission originating from electronic states within the bandgap of TiO₂ is observed. These states are assigned to defects due to oxygen vacancies in the TiO₂ lattice. At the highest O₂ pressure, the defect state photoemission signal disappears, indicating a defect free lattice. As the pressure is varied, a shift in the photoemission onset of the O 2p electronic states is observed, with a shift of 20 meV towards the Fermi level. The defect states in TiO₂ can be engineered and controllably generated using the deposition/growth technique.

To assess the influence of defects on the charge transfer process, the time resolved pump-probe scheme was employed. The electrons in p-Si(100) are excited using an 800 nm pulse, while photoelectrons are generated at variable delay times by the XUV probe pulse. Transient shifts in the kinetic energy (binding energy) of photoejected electrons are observed when either there is an influx of electrons around an element, manifested as an increase in kinetic energy (decrease in binding energy) of photoelectrons from the element's core level, or an absence of electrons, having the opposite effect on the element's core level binding energy. Thus, by varying the delay between these two beams, time-dependent dynamics can be observed for the electron distribution.

Transient photoemission measurements (Fig. 3) for the defect rich TiO₂ (grown at 8×10^{-9} Torr O₂ pressure) show clear shifts (red line) in the binding energy of the O 2p photoelectrons in the TiO₂ layer (cf. Fig. 2, where the dotted line shows the valence band maximum position via the O 2p electrons without photoexcitation), corresponding to electron injection from the silicon to the surface of the TiO₂. However, the defect free TiO₂ sample (blue line, grown at 10^{-6} Torr O₂ pressure) shows no change in the photoemission signal, indicating that the electron density in the TiO₂ surface layer is unaffected by excitation of the p-Si(100) substrate. This behavior is

rationalized by the band structure of the two samples (Fig. 4). In the defect free case, the conduction band of TiO_2 is slightly higher in energy than the conduction band of p-Si(100). This results in blocking of electron injection into TiO_2 , and thus the lack of photoemission response. For defect rich TiO_2 , the conduction band is below the p-Si(100) conduction band, which facilitates electron injection. Observation of defect dependent behavior sheds light on the effect of defects on band alignment and, subsequently, electron dynamics. Furthermore, this points to the importance of fundamentally understanding the consequences of defect concentration on electron dynamics in photocatalyst design.

2.2 Schottky Barrier Junctions

Metal-semiconductor junctions have found uses ranging from electronics to enhancing

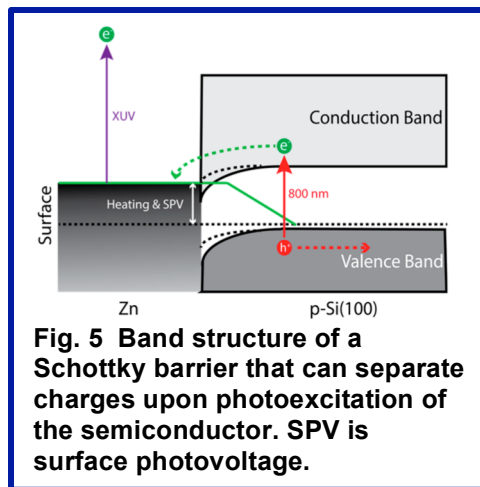
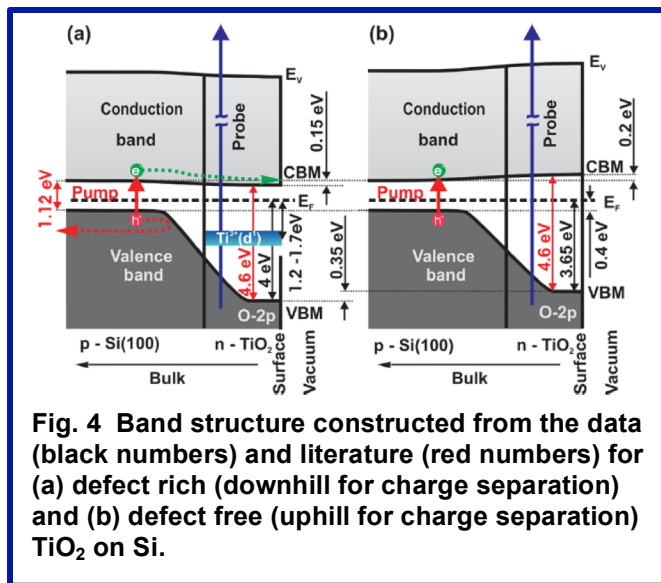
photocatalytic reactions. When a metal-semiconductor contact is formed, the junction is either ohmic or rectifying in nature. In the case of an ohmic contact, the junction shows no resistance to current flow in either the positive or negative direction.

For a rectifying junction, the current flow is blocked in one particular direction (Schottky barrier), based on the characteristics of the semiconductor material used (Fig. 5). This case, referred to as a Schottky junction, allows for separation of electrons and holes between the metal and semiconductor layers. This can result in longer carrier lifetimes at metallic co-catalysts, leading possibly to enhanced photocatalytic activity.

2.2a Thermalization and recombination observed in

Zn on p-Si

To study the carrier dynamics in a model junction system, 3.5 monolayers (ML) of Zn were grown on a p-Si(100) substrate at cryogenic temperatures (~ 90 K). Previous electrical characterization of this junction indicated that the contact is rectifying in nature, meaning that the



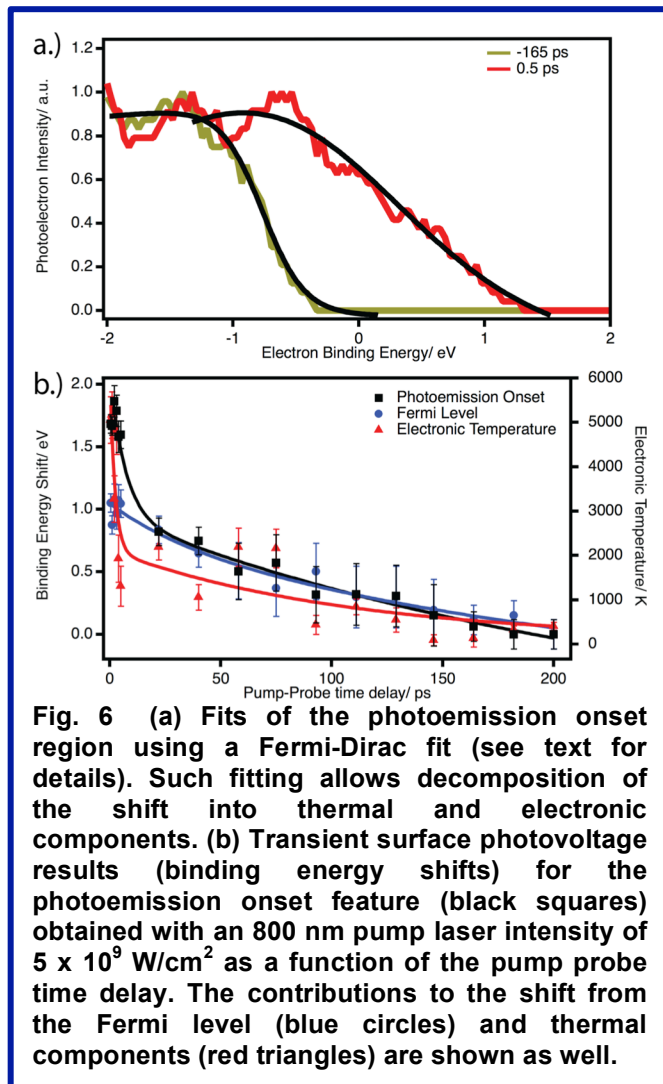


Fig. 6 (a) Fits of the photoemission onset region using a Fermi-Dirac fit (see text for details). Such fitting allows decomposition of the shift into thermal and electronic components. (b) Transient surface photovoltage results (binding energy shifts) for the photoemission onset feature (black squares) obtained with an 800 nm pump laser intensity of $5 \times 10^9 \text{ W/cm}^2$ as a function of the pump probe time delay. The contributions to the shift from the Fermi level (blue circles) and thermal components (red triangles) are shown as well.

Decomposition of the photoemission onset feature using a Fermi-Dirac distribution requires two components (Fig. 6): a change in the Fermi level energy and the electronic temperature. The result of this decomposition is shown in Fig. 6b. The Fermi level component decay (black points) is found to be biexponential in behavior, with components of $36 \pm 10 \text{ ps}$ and $300 \pm 70 \text{ ps}$, while the electronic temperature decay (red points) is also biexponential, with components of $2 \pm 1 \text{ ps}$ and $110 \pm 70 \text{ ps}$. Comparing the Fermi level and electronic temperature shifts to the overall photoemission onset shift shows that at early times the dynamics are dominated by thermalization of the electrons in Zn, while the later time features are due to recombination of electrons and holes, both of which lead to decreases in the Fermi level energy and further decreases in the electron temperature.

flow of holes to the surface is forbidden under normal conditions. Auger electron spectroscopy measurements performed here indicate that the growth proceeds in a layer-by-layer (Frank-van der Merwe) fashion and the photoemission measurements indicate the electronic structure of the film is metallic.

Excitation of the junction with an intense 800 nm pump pulse, followed by the time-delayed XUV probe pulse, shows that immediately after excitation the photoemission onset displays a shift to lower binding energy and the Zn 3d core level undergoes a similar shift, as well as broadening. The shifts indicate that electron density is being added to the Zn overlayer, as expected from the previously determined electronic structure of the junction.

The results show that the Zn 3d core level shifts are sensitive to the electron temperature, which is a valuable new finding. The similarity of the photoemission onset dynamics to the dynamics observed in the Zn 3d core level indicates that the core level electrons can report on the electron energy distribution or temperature of the valence electrons. This discovery opens the door to

performing core level, and therefore element specific, transient photoemission investigations that can resolve electron temperatures in valence and conduction band states in the future.

2.2b Band bending in Zn on n-GaP(100)

To further understand carrier dynamics in junction systems, Zn on n-GaP(100) , a system in which both layers can be probed simultaneously during transient measurements was selected. In

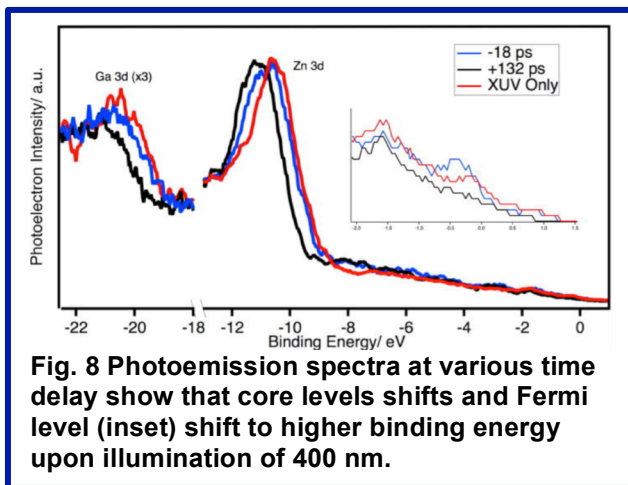


Fig. 8 Photoemission spectra at various time delay show that core levels shifts and Fermi level (inset) shift to higher binding energy upon illumination of 400 nm.

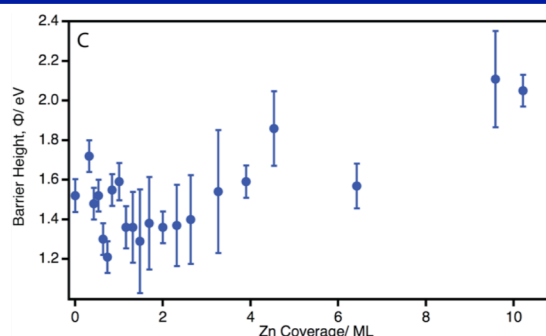
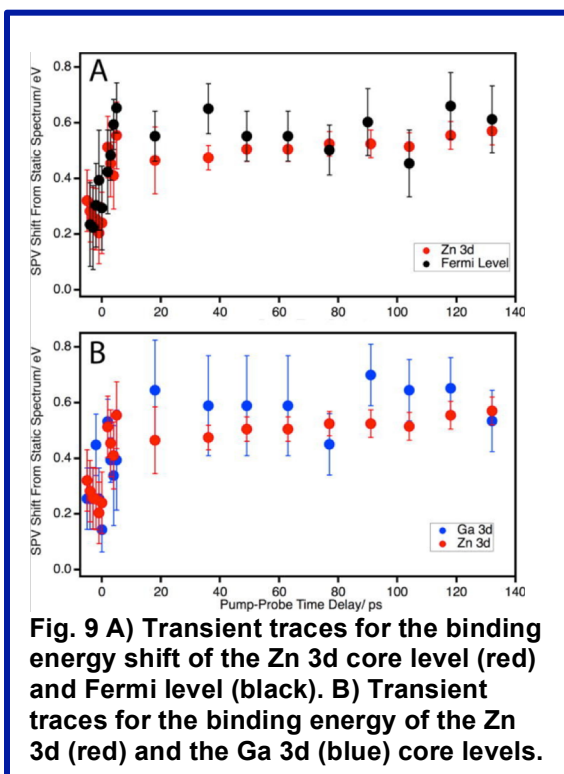


Fig. 7 Measured Schottky barrier height for various amounts of Zn deposited onto n-GaP(100).

the same method as was mentioned previously, it was observed through Auger electron spectroscopy measurements that thermally evaporated Zn onto GaP(100) grows in a Stranksy-Karastanov (forming a single monolayer and then particles) mode. In other works, it has been known that Zn on n-GaP forms a rectifying junction in which holes accumulate on the surface. Through static photoemission measurements in this

study it was observed that 10 apparent ML (on average ~2.8 nm thickness) of Zn grown on n-GaP(100) at room temperature forms a Schottky barrier of 2.1 ± 0.1 eV (Fig. 7).

Upon excitation of a 400 nm pump at positive time delay (in which the pump arrives before the probe), it was observed that the both the Ga 3d and Zn 3d core levels as well as the Fermi level shifted toward higher binding energy, indicating that holes accumulate at the surface and within the first few crystal planes of the GaP (Fig. 8). Secondly, it was observed when comparing negative time delays (in which the probe arrives before the pump) to the static



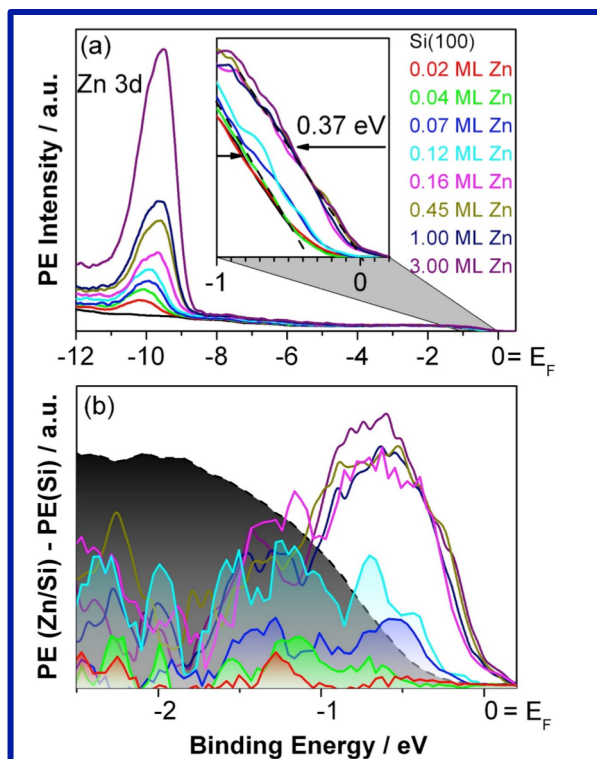
binding energy shift within the Zn layer, and the depletion region of the GaP is likely the same. From these findings it is clear that as holes are shuttled to the Zn surface layer the electric field in the n-GaP depletion region is screened, ultimately resulting in a lowering of band bending. This finding shows that it is possible to use transient XUV photoemission to monitor dynamics within the surface layers and depletion region of junction systems.

2.3 Size dependent dynamics in Schottky junctions

While Schottky contacts are often utilized in photocatalytic systems, it is usually in the context of small metallic particles or clusters on semiconductors, as opposed to metallic films. Previously, transient measurements indicate that

photoemission that the both core levels were shifted ~ 0.2 eV toward higher binding energy (Fig 8). This confirms the presence of long lived (~ 1 ms) carriers, which has previously been observed through surface photovoltage measurements of various metals on n-GaP.

All three of the features, the Fermi level, Ga 3d core level, and Zn 3d core level, appear to have similar time-scales and magnitudes to the observed shift (Fig. 9). This indicates that the underlying dynamic process causing the observed



the size of particles can influence the recombination dynamics of carriers in the system. This is believed to have significant effects on the catalytic activity, leading to interest in optimizing nanostructures for peak performance.

To assess the effects of metal particle size and coverage on recombination dynamics the electronic structure of Zn on p-Si(100) at various coverages is first investigated using static XUV photoemission measurements. The resulting spectra, shown in Fig. 10, indicate that as the Zn coverage is increased, the Zn 3d core level spectral feature at -10 eV binding energy grows in and shifts to lower binding energies. Closer examination of the photoemission onset region shows that for coverages from 0.02 ML to 0.12 ML Zn the photoemission onsets are near the photoemission onset of p-Si(100). However, for coverages of 0.16 ML and above there is a clear shift of ~ 0.4 eV toward the Fermi level, indicating that the Zn layer is metallic in nature. Previous measurements of Zn clusters on Si with scanning tunneling microscopy reveal that the

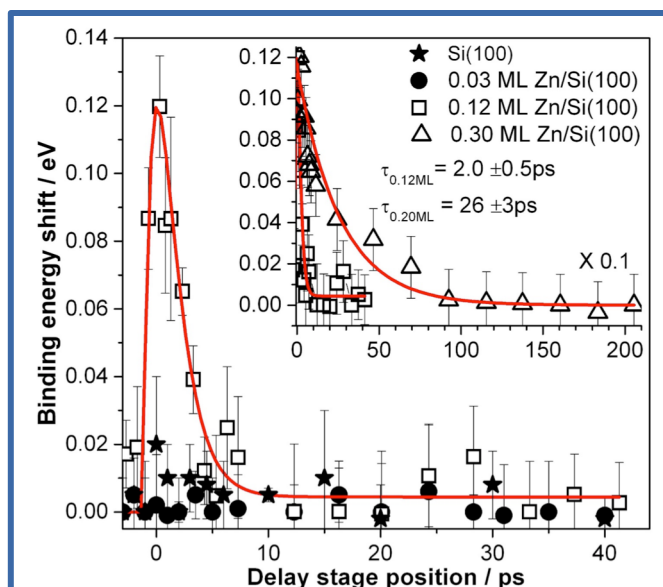


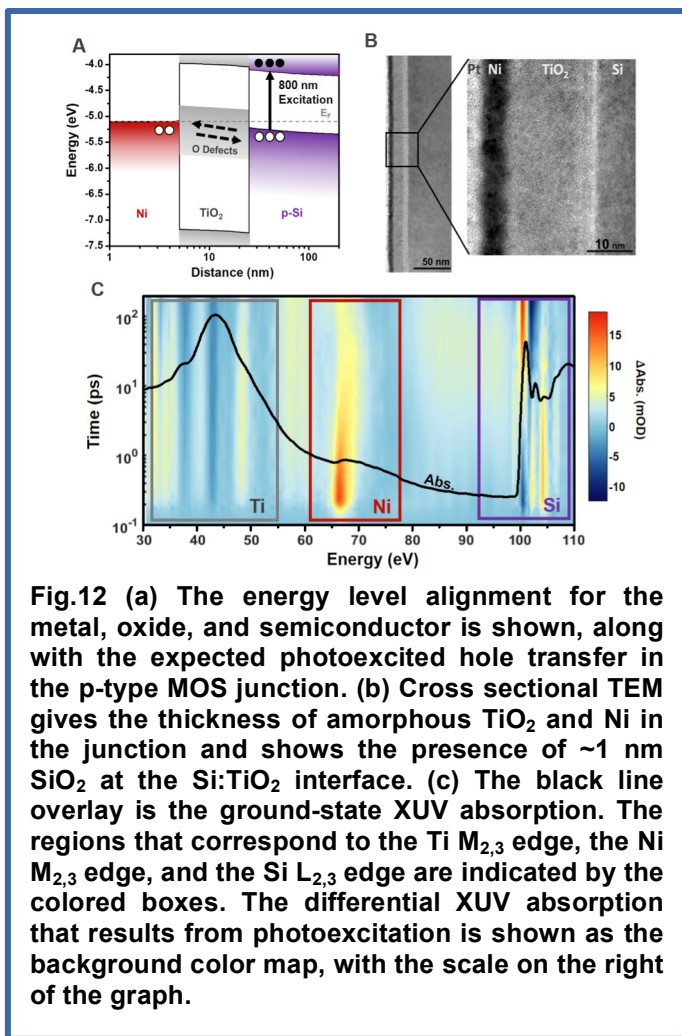
Fig. 11 Ultrafast charge carrier dynamics at the surface of a p-Si(100) surface decorated with Zn clusters. Transients obtained from 0.03 ML Zn on Si(100) (filled circles), 0.12 ML Zn/Si(100) (squares) and 0.2 ML Zn/Si(100) (triangles) by monitoring the shift of the Zn 3d photoemission peak as a function of the pump (800 nm) - probe (23rd harmonic) time delay. A transient signal obtained from the bare Si(100) by monitoring the valence band maximum of p-Si(100) under identical investigation conditions is included as a reference (stars).

growth first occurs in dimers and trimers, then rows, and finally two-dimensional platelets. From our work, at a certain size, the Zn clearly becomes metallic, without having complete coverage. It is also notable that the Zn 3d core level shift moves from higher binding energies in the non-metallic clusters, to lower binding energies, and finally to the bulk Zn 3d binding energy, as the clusters become metallic in nature (Fig. 10a). This is indicative of interactions between the Zn atoms and the Si substrate dominating at low coverages and Zn-Zn interactions becoming more important at higher coverages. While the electronic structure (i.e. metal vs. non-metal character) influences carrier recombination, it is not the only factor that plays into the carrier

dynamics, as discussed further below.

The dynamics of electrons in these semiconductor-metal cluster junctions were investigated using the pump-probe scheme for Zn coverages of 0.12 ML and 0.2 ML on p-Si(100) (Fig. 11). In the case of 0.12 ML coverage, the electrons are observed to enter the Zn layer and quickly recombine with holes in the substrate (< 10 ps). Since Zn is non-metallic at the 0.12 ML coverage, a Schottky barrier is not successfully formed and electrons cannot be trapped in the Zn cluster. Thus, the electrons are transferred back into the p-Si(100) substrate immediately after excitation. In the case of the metallic 0.20 ML coverage, the electron lifetime in Zn is an order of magnitude longer, and the Zn 3d binding energy shift is also significantly larger, indicating 1.) a barrier to recombination has formed and 2.) that more electron density is trapped at the Zn particles than in the 0.12 ML case. This is attributed to the metallic character of

the 0.20 ML Zn particles. In that case, even though the metal layer is formed into small clusters, a Schottky barrier is established, which results in diminished recombination of the electrons in Zn with holes in the p-Si(100), thus lengthening the lifetime as well as increasing the number of electrons that can remain at the surface. These results show the efficacy of time-resolved XUV-PES as an electronic structure tool for characterizing surfaces, as well as providing crucial information about the size dependent behavior of carriers in Schottky junction systems.

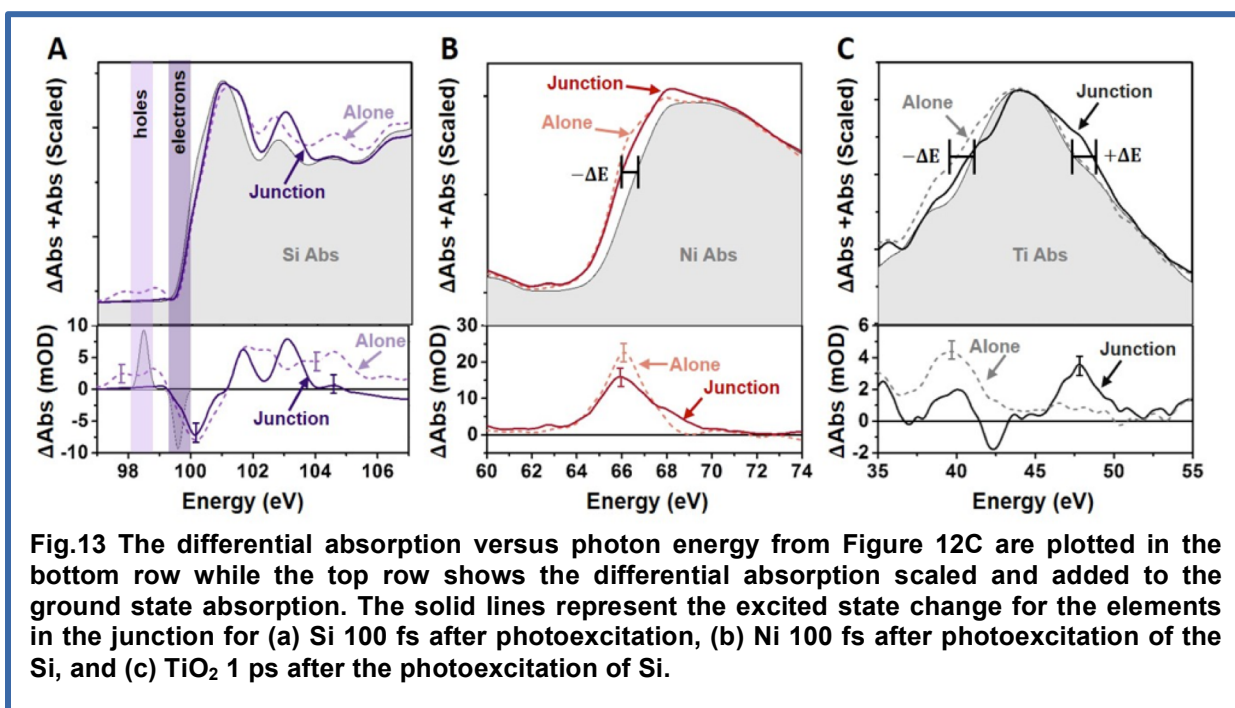


2.4 Charge Transfer Kinetics of Metal-oxide-semiconductor Passivated Systems

Metal-oxide-semiconductor (MOS) passivated junctions have garnered much attention in solar energy research. The use

of these layered junctions in solar cells and photoelectrodes have led to high photoconversion efficiencies. Slowing surface recombination velocity, adding a corrosion barrier, and aiding in proton transport are some of the benefits gained from using MOS passivated junctions in solar cells, for CO₂ reduction, and as photoelectrodes. It has been shown that thicker, amorphous, and defect-rich oxide layers often outperform crystalline, thinner barriers. XUV transient absorption is used to observe the underlying hole transfer in a Ni-TiO₂-Si junction in order to better understand the performance enhancing effects of including the metal-oxide layer that has been observed in junction systems.

The junction system was created by taking a 200 nm thick p-Si membrane and thermally



evaporating Ti under a low oxygen atmosphere (8×10^{-9} Torr O₂ pressure) to create a 19 ± 0.6 nm thick, defect rich TiO₂ layer. Then 5.6 ± 0.6 nm of Ni was deposited on top of the TiO₂ (Fig. 12B). The transient absorption spectrum of this junction sample contains three main features, the Ti M_{2,3} edge, the Ni M_{2,3} edge, and the Si L_{2,3} edge (Fig. 12C).

By comparing transient absorption measurements on the junction to each single component alone, specifically a Si membrane, TiO₂ on a diamond membrane, and Ni on a diamond membrane, dynamics that are purely a part of the junction can be actualized. In Si there is a pronounced electron signal observed at ~ 98.5 eV as well as increased oscillatory feature above 101 eV due to increased lattice heating when comparing the junction to the non-junction

Si (Fig. 13A), but there is a distinct absence of holes, which have transferred to another layer. The Ni in the junction shows a significant edge shift indicative of hole transfer at very early times, indicating that the holes in Si have transported to the Ni (Fig. 13B). The TiO₂ in the

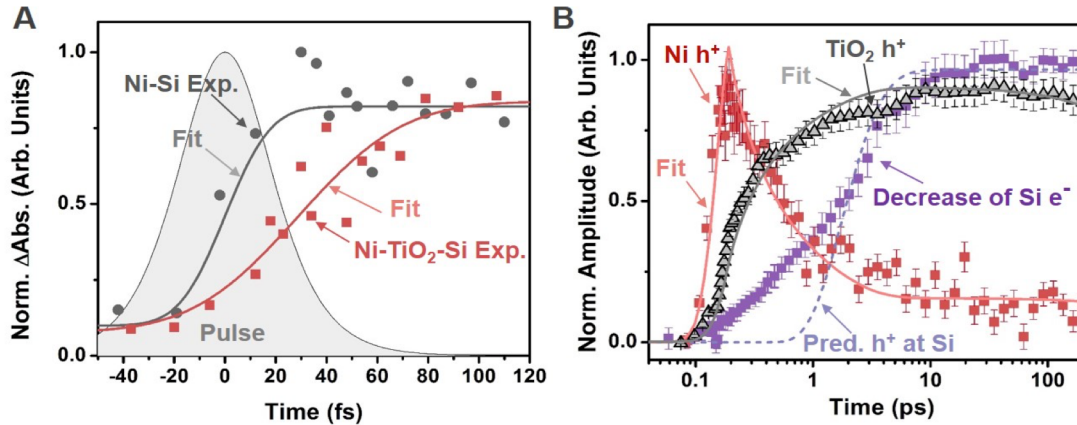


Fig.14 (a) The square light red symbols represent the magnitude of the measured rise time of the Ni edge in the junction. The grey circles represent the rise time of the Ni in a Si-Ni junction with no TiO₂ spacer. Fitting the experimental data to an error function (solid lines). **(b)** The edge shift kinetics measured for the TiO₂ (grey triangles) and the Ni (red squares) in the junction are compared to the increase in electron recombination (or decrease in electron signature at the Si edge) in the junction (purple squares). The solid line is a fit to the diffusion equation with a diffusion constant of $1.2 \pm 0.1 \text{ cm}^2/\text{s}$ and a surface recombination velocity of $200 \pm 50 \text{ cm/s}$.

junction shows a slower edge shift in the opposite direction to TiO₂ alone, also indicative of hole transfer on later times (Fig. 13C).

It is clear from initial analysis of the transient measurement that the hole feature in Si and the Ni edge shift both appear immediately after excitation, while no edge shift is observed in the TiO₂ until after 1 ps (Fig. 12 C). This indicates that holes transfer from Si to Ni within the first 100 fs of excitation. In order to quantify carrier kinetics, each time point of the optically excited data was fit as equilibrium changes to the ground state. By fitting the magnitude of the MOS junction Ni edge rise, time-convoluted with the 50 ps pump pulse width and comparing this result with a Ni-Si junction, it was found that the arrival of holes in the TiO₂ layer is delayed by $33 \pm 2 \text{ fs}$ (Fig. 14A). From this an average tunneling hole velocity and mobility were calculated to be $5.8 \pm 0.4 \times 10^7 \text{ cm/s}$ and $380 \pm 40 \text{ cm}^2/\text{V}\cdot\text{s}$, respectively. Because the calculated tunneling hole mobility is similar to that of p-Si ($495 \text{ cm}^2/\text{V}\cdot\text{s}$) and there is a lack of measurable hole signal in TiO₂ during the initial tunneling, the hole transport through the TiO₂ layer is suggested to be ballistic in nature. From fitting the Ni Fermi level change and accounting for the optical excitation density, a hole injection efficiency is quantified as $42 \pm 6\%$. Finally, by fitting the Ni

and Ti edge shifts, which represent hole kinetics, with the diffusion equation, a hole back diffusion constant of $1.2 \pm 0.1 \text{ cm}^2/\text{s}$ is obtained (Fig. 14B). Overall, these measurements and calculations show that XUV transient absorption is a versatile analysis tool capable of measuring charge transfer in complex junction systems.

Publications acknowledging AFOSR support 2014-2019

S. D. Chambreau, A. C. Schenk, A. J. Sheppard, G. R. Yandek, G. L. Vaghjiani, J. Maciejewski, C. J. Koh, A. Golan, and S. R. Leone, "Thermal decomposition mechanisms of alkylimidazolium ionic liquids with cyano-functionalized anions," *J. Phys. Chem. A* **118**, 11119 (2014).

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Abstract

A strategy that has found much success for semiconductor photocatalysis involves the creation of junctions of semiconductors with metals, either as thin films or as particles. Such materials are often observed to possess significantly higher activities and corrosion resistances when compared to a semiconductor alone. Understanding the effect of metal deposition on photocatalysts requires an understanding of the electronic structure of the junction as well as the behavior of the electrons and holes generated by solar radiation. In this report, A new apparatus has been constructed that produces extreme ultraviolet ultrafast laser pulses, which can be used for time resolved photoemission. Static spectra reveal the growth modes of metals on semiconductors and time-resolved studies show photovoltage shifts that reveal the dynamics of electron or hole carriers moving from one layer into another. In several studies, zinc junctions on silicon [Si(100)], both films and nanoparticles,

and a Zn/n-GaP(100) junction were studied using the ultrafast time-resolved extreme ultraviolet (XUV) photoemission technique. The approach to metal character was revealed versus the size of the particles. Schottky barrier principles were elucidated, including new results demonstrating that core level transitions can reveal the changes in electron temperature in the same way as changes in Fermi electron distributions do. Using XUV transient absorption to look through a junction, layer-specific time-resolved results are obtained for the hole transport across a Si-TiO₂-Ni photoanode junction. The results indicate that the XUV photoemission and transient absorption techniques are highly suitable for studying the carrier dynamics of a wide range of junctions.

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