

ERIC BORGUET, RESEARCH ACCOMPLISHMENTS AND FUTURE DIRECTIONS

“Structure, Dynamics and Reactivity at Interfaces”

Nanotechnology is one of the most interesting and challenging frontiers of science and technology. We are motivated by the belief that progress will come from improved understanding and control of structure, dynamics and reactivity at interfaces. First, we provide a summary of our projects and key findings. The following pages provide a more detailed account.

Charge Transfer, Trapping & Dynamics at Interfaces

Our group is exploring strategies to link the world of organic chemistry to that of solid supports. We use chemistry to control, and nonlinear optics to investigate, the dynamics of electrons near ultra thin dielectric layers at semiconductor interfaces. Key findings include

- The nonlinear optical susceptibility of Ge conduction band is $\sim 1,000\times$ greater than valence band.[1]
- Surface functionalization (-Cl, -S) accelerates carrier thermalization at Ge interfaces.[2]
- High-K dielectrics show significantly reduced detrapping of injected charges compared to SiO_2 . [3]
- Electronic structure of well-prepared Si(111)-H surfaces can be stable for up to a week.[4]

Photochemical Dynamics and Reactivity of Siloxane SAMs

We develop new methods of identifying different surface functional groups and apply them to study the mechanisms of oxidation of siloxane self-assembled monolayers (SAMs). Key findings include

- Contrary to alkanethiol SAMs, ozone is not the active agent in photodegradation.[5]
- New surface analytical tool Fluorescence Labeling of Surface Species (FLOSS) was developed.[6]
- Detection limit of FLOSS reduced to $\sim 10^9/\text{cm}^2$ (~ 10 groups/ μm^2).[7]
- Demonstrated growth of siloxane SAM on piezoelectric substrate (LiNbO_3).[8]

Surface Chemistry of Carbon Nanotubes and other Nanoporous Carbon Materials

We are identifying the roles of surface chemical functionality and topology in determining behavior of nanoporous carbonaceous materials, including single-wall carbon nanotubes (SWNTs). Key findings include

- Experimental (IR) evidence that NH_3 adsorption on SWNT is functional group/defect mediated.[9]
- Surface specificity of FLOSS identifies functional groups on activated carbon fiber surfaces.[10]
- FLOSS identifies nature and quantity of oxygen containing functional groups on CNTs.[11, 12]
- Interaction energy of acetone with different adsorption sites of SWNTs was determined.[13]
- Adsorption conditions strongly influence the accessibility of certain adsorption sites on SWCNTs.[14]

Ultrafast Laser Spectroscopy of Interfaces and Development of Ultra-Broadband Pulsed Laser Sources

We use a surface-specific spectroscopy technique, Sum-Frequency Generation (SFG), to investigate ultrafast vibrational energy relaxation and dissipation at interfaces. We also develop new sources of ultra-broadband pulses for spectroscopic applications. Key findings include

- Combination of time- and frequency domain SFG spectroscopies of siloxane self-assembled monolayers (SAMs) allows investigation of disordering introduced into SAM structure.[15]
- Observation of weakly- or non-hydrogen bonded OH groups at the mineral CaF_2 -water interface at high pH suggests hydrophobization of the mineral surface.[16]
- Vibrational energy flow through water molecules at interfaces is strongly affected by surface charge induced ordering as revealed by ultrafast infrared pump – SFG probe studies.[17]
- Generation of near-IR pulses with bandwidth $>2500\text{ cm}^{-1}$. [18, 19]
- Generation of infrared pulses with bandwidths $\geq 1500\text{ cm}^{-1}$ in the $\sim 2\text{-}3\ \mu\text{m}$ wavelength region.[20]

We believe that the novel phenomena that we have discovered shed light on the fundamental properties of technologically important interfaces.

1. Charge Transfer, Trapping & Dynamics at Semiconductor Interfaces

Second Harmonic Spectroscopy of Chemically Modified Semiconductor Interfaces

The ambient stability of semiconductor surfaces is a key to their usefulness. We focus on novel organic and inorganic passivation layers, not only for silicon but also for germanium.

We have investigated the stability of the H terminated Si(111) surface and the kinetics of oxide regrowth in ambient (Fig. 1) and under photo-irradiation (Fig. 2) by *in-situ* SHG experiments.[4, 21] We have demonstrated that the interfacial electronic structure of well prepared Si(111)-H, as determined by SHG, can be stable for $>10^4$ minutes! [4] (Fig. 2) However, intense laser illumination can lead to accelerated, photon-driven reactivity (Fig. 2) that can be harnessed for useful ends, e.g, photografting of organic species or photolithography.

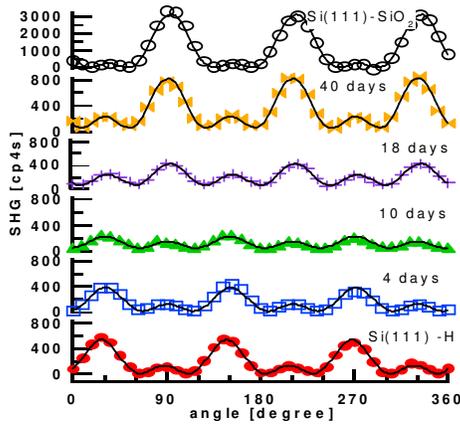


Fig. 1 SHG rotational anisotropy tracks the ambient oxidation of Si(111)-H.[4, 21]

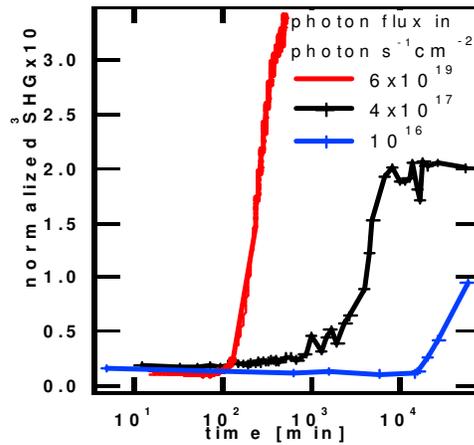


Fig. 2 SHG response to photo-induced Si(111)-H oxidation.[4]

Germanium offers a number of advantages, e.g., higher carrier mobility, and has a potential to replace and/or complement silicon provided that several obstacles can be overcome. Our SHG pump-probe studies of Ge(111)/GeO₂ interface showed that the nonlinear susceptibility of charge carriers excited by a short laser pulse becomes ~ 900 times greater than that of valence-band carriers within few picoseconds after excitation.[1] This ratio is an order of magnitude greater than that for Si(111)/SiO₂. However,

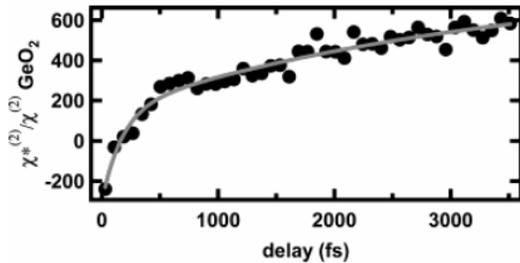


Fig. 3 Evolution of the ratio of nonlinear susceptibilities of hot carriers to valence-band carriers for the Ge(111)/GeO₂ interface.[1]

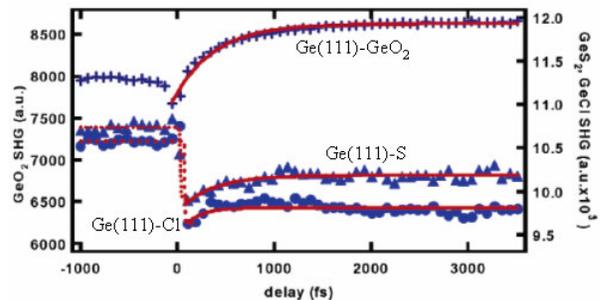


Fig. 4 Ultrafast SHG from Ge(111)-GeO₂, Ge(111)-S and Ge(111)-Cl.[2]

unlike SiO₂, the native oxide of Ge is water soluble, limiting its usefulness. Exploiting Ge surface chemistry to produce a stable passivating layer may help define new applications. SHG clearly enables

different surface terminations to be distinguished (Fig. 4), providing an *in-situ* probe of chemical transformation of these surfaces.[2] Consistent with IR-SHG results, our recent experiments reveal significant effects of surface chemistry on interfacial carrier thermalization at Ge interfaces.[1, 2]

We have collaborated with IBM to understand the influence of interface structure/chemistry on the properties of $\text{Si}_{1-x}\text{Ge}_x$ interfaces, especially the roles of fixed charge, charge tunneling and accumulation in the development of alternative organic and inorganic (ZrO_2 , HfO_2 ...) ultrathin dielectric layers, under consideration for the next generation of devices and molecular electronic applications.[3] In particular, time-dependent SHG measurements showed that Al_2O_3 films grown on silicon slides have the highest densities of trapped and fixed charge. Additionally, detrapping in the high-K dielectrics, contrary to SiO_2 films, is significantly suppressed.

2. Photochemical Dynamics and Reactivity of Siloxane SAMs

The photochemistry of alkylsiloxane SAMs, potential dielectric and photoresist material for semiconductor applications, has yielded remarkable results.[5] Contrary to alkanethiol SAMs, ozone is not the active agent in photodegradation. The combined action of UV photons and oxygen species is required to remove siloxane SAMs. Steric factors play an overwhelming role in determining the reactivity of different chemical groups in the ODS SAM; the more accessible CH_3 group appears to be consumed before the CH_2 groups.

In order to detect reaction intermediates, and reveal the mechanism of this process, we developed a novel surface analytical tool FLOSS (Fluorescence Labeling of Surface Species).[6] FLOSS exploits the sensitivity of fluorescence and the specificity of covalent bond formation to identify and quantify low concentrations of surface functionalities (Fig. 5).[7] FLOSS can be applied to a variety of surfaces to distinguish between COOH , OH and CHO groups, and we have quantified the specificity of FLOSS via the competing reaction with amino groups between COOH and CHO (~1:500) (Fig. 6).[7] FLOSS can now detect down to 10^9 functional groups/ cm^2 on the surface, which is well beyond the detection limits of FTIR and XPS.[7]

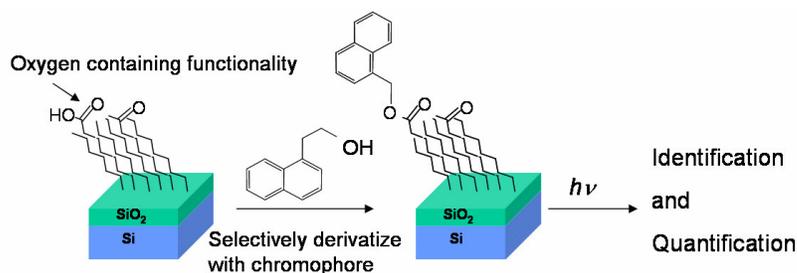


Fig. 5 The scheme of FLOSS. The oxygen containing functional groups on SAM surface are labeled with fluorescent molecules. Surface fluorescence detection is performed to identify and quantify the functional groups on the SAM surface.[5, 6]



Fig. 6 The post reaction cleaning procedure is effective to remove ionically bonded dyes on the surface. The presence of carboxyl groups on the surface will not affect the detection of aldehyde groups using amino modified dye.[7]

Self-Assembled Monolayer Compatible with Metal Surface Acoustic Wave Devices on Lithium Niobate
Surface acoustic wave (SAW) devices have been utilized for a wide range of applications such as mobile communication systems, and chemical sensors. It is tempting to combine the small, wireless features of

SAW devices with self-assembly techniques to control the wettability of the device to achieve controlled deposition of a metal layer or to achieve direct grafting of biopolymer- and polymer-sensing materials or even the design of more complex nanostructures.

We have investigated the formation of siloxane self-assembled monolayers (SAMs) on LiNbO_3 , which acts as piezoelectric substrates in SAW devices, with aluminum as an electrode. The most widely used coupling reagent, Octadecyltrichlorosilane (OTS), etches Al metal features due to the formation of high local concentrations of hydrochloric acid. On the other hand, an alternative coupling reagent, octadecyltrimethoxysilane (OTMS), does not show any etching of metal parts (Fig. 7). This SAM has characteristics that make it compatible with conventional SAW device manufacturing techniques.[8]

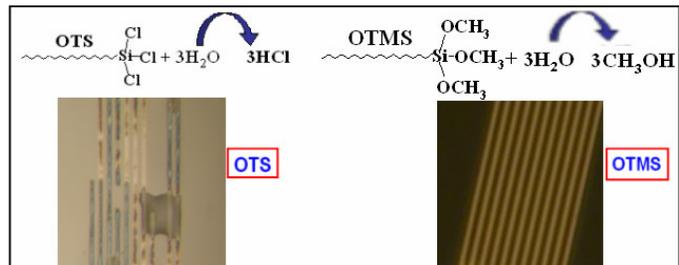


Fig. 7 Typical microscope image of an Al device on LiNbO_3 after OTS and OTMS treatment.[8]

This SAM has characteristics that make it compatible with conventional SAW device manufacturing techniques.[8]

3. Surface Chemistry of Carbon Nanotubes and other Nanoporous Carbon Materials.

Nanoporous carbon materials, e.g., carbon nanotubes (CNT), are the object of intense study. Key to many

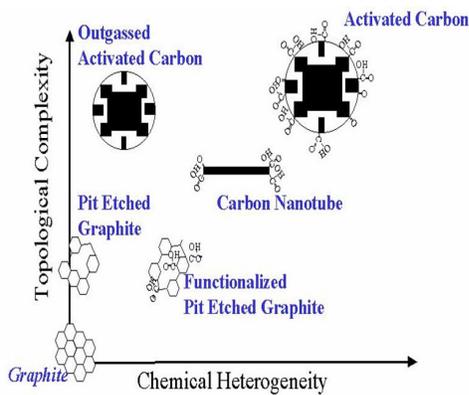
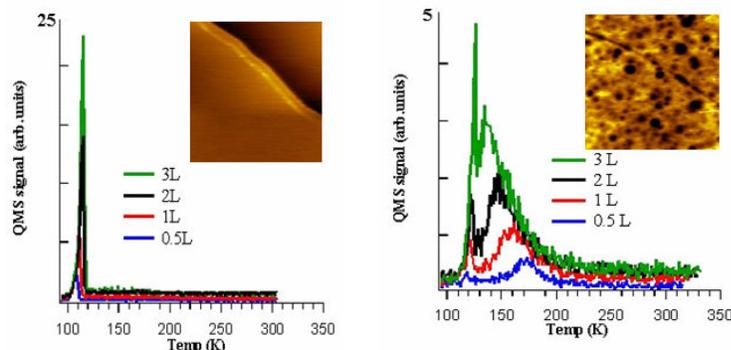


Fig. 8 Carbonaceous materials are characterized by nature and degree of topology and chemical functionality.[22]

applications, e.g. sensors, is the interaction of nanoporous carbons with molecules. We are interested in the effect of chemical and topological heterogeneity on the properties of nanoporous carbons (Fig. 8).[22] Applications can involve pressures from UHV to atmospheric, requiring the development of appropriate probes to bridge this pressure gap to determine absolute coverage for physisorbed species and investigate surface kinetics on carbonaceous surfaces.[22-24]

Chemical groups and surface morphology/topological complexity (Fig. 8) have important effects on adsorption/desorption on carbonaceous surfaces.[23] Oxygen containing functional groups, that exist on air cleaved HOPG, plasma oxidized HOPG and SWNT, can reduce the capacity and slow the adsorption kinetics for a model non polar organic adsorbent (propane) (Fig. 9). [23]

The unexpected presence and effects of surface functionality on HOPG surfaces has been confirmed by other researchers. Removal of these groups leads to over an order of magnitude increase in propane adsorption capacity.[23] Introducing surface chemical and topological heterogeneity (Fig. 9) can be used to optimize the surface properties of high surface area nanoporous carbons used in practical applications. Similarities between Fig. 9(b) and Fig. 10 suggest that nanopores formed by plasma oxidation of HOPG can serve as a useful model system of CNT.



(a) Air Cleaved HOPG (b) Plasma oxidized HOPG
 Fig. 9 TPD of propane from (a) air-cleaved and (b) plasma oxidized HOPG, initially heated to above 1273K to remove surface functionality (most likely polar oxygen containing groups). Clearly, Fig. 9(b) reflects morphological heterogeneity of plasma oxidized HOPG providing new, higher energy sites for adsorption. Insets: AFM images ($\sim 3000 \times 3000 \text{ nm}^2$).[23]

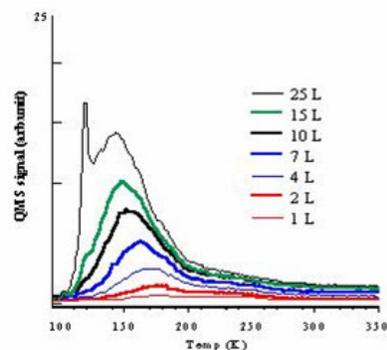


Fig. 10 Propane TPD from single-walled CNT deposited on air-cleaved HOPG. System was heated to 1273 K before TPD to remove chemical functional groups.

Our CNT experiments reveal how purification introduces functionality, and the fate of the functionality upon thermal treatment (Fig. 11).[25] We have also recently shown that NH_3 adsorption appears to be functionality/defect mediated and that pristine single-walled CNTs show no sign of adsorption of ammonia (Fig. 12).[9] These results have important consequences for CNT based devices. Given the clear importance of oxygen containing functionality we are extending our FLOSS technique to carbon materials including activated carbon fibers, and carbon nanotubes.[11]

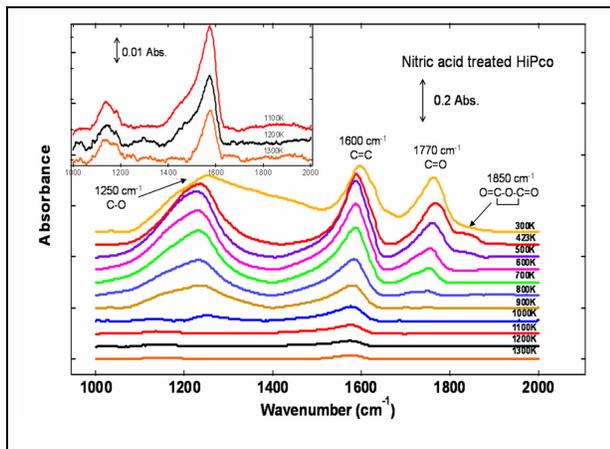


Fig. 11 IR peak evolution of nitric acid treated HiPco samples during vacuum heating from 300K to 1300K. [25]

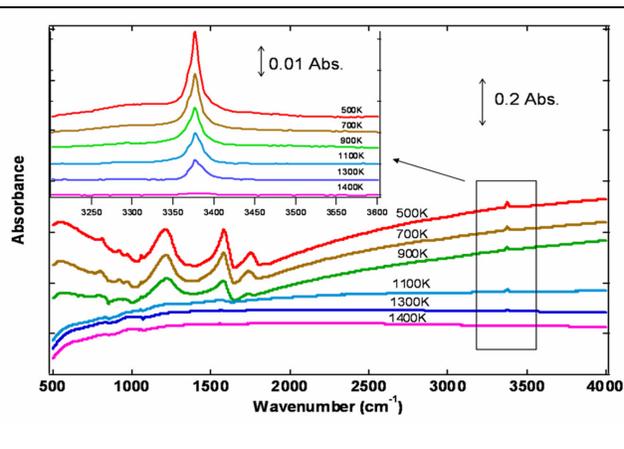


Fig. 12 IR of Ammonia adsorption at 94K on nanotubes treated to successively higher temperatures, a process that drives off surface functionality and heals defects. [9]

Carbon nanotubes have potential applications as sensors. Adsorption of gases on nanotubes can significantly differ from adsorption on conventional materials because nanotubes introduce nanometer-scale confinement of target gases. Our recent TPD studies of acetone adsorption on SWNTs revealed at least three possible adsorption sites (Fig. 13(A)).[13] TPD of acetone from SWNTs show an intense peak at $\sim 300\text{K}$, which is not present in TPD of acetone from carbon black (Fig. 13(B)). We relate this peak to desorption of acetone from endohedral sites of small-diameter ($\sim 7\text{-}10 \text{ \AA}$) nanotubes.

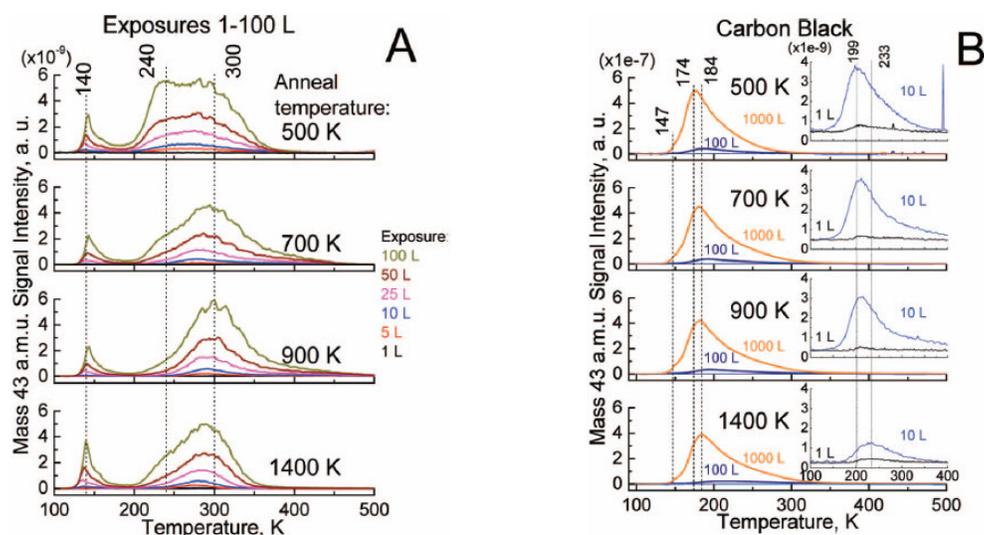


Fig. 13 (A) Desorption of acetone (mass 43 a.m.u. (CH_3CO fragment)) from purified SWCNTs annealed to 500, 700, 900, and 1400 K prior to adsorption, at acetone exposures 1-100 L. Sites with three different adsorption energies ~ 35 (desorption peak at 140K), 50 (peak at 240K), and 75 kJ/mol (peak at 300K) appear to be present on SWCNTs. The acetone uptake by each site depends on the SWCNT anneal temperature. (B) For comparison, TPD of acetone from carbon black (same adsorption conditions) is shown. Two desorption peaks can be detected for carbon black: small shoulder at 140–150 K and intense peak at 180–240 K; no peak at ~ 300 K was observed.[13]

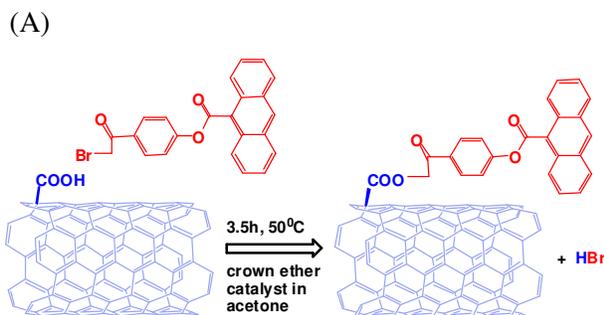


Fig. 14 FLOSS labeling reaction schemes for carboxylic groups with panacyl bromide (A); similar schemes were used for carbonyl groups with dansyl hydrazine ; alcohol groups with 5-DTAF (C).[12, 28]

chemical groups (Fig. 14).[28] The results show that nitric acid treatment, a quite aggressive procedure, introduces ~ 5 times more functional groups than Air/HCl treatment, and ~ 10 times more functional groups than the non-treated SWCNTs have. Interestingly, it is the carbonyl, not the carboxylic, groups that are the most abundant.[12, 28] This suggests that SWCNTs derivatization routes should exploit the chemistry of carbonyls rather than carboxylic groups. We plan to extend FLOSS to a wider spectrum of the functional groups (e.g amino groups, ethers) and other types of the carbon materials (e.g. Multiwalled Carbon Nanotubes, Carbon Blacks). We also plan to develop a chemical microscopy based on FLOSS to reveal nanometer scale chemical composition of complex materials.

The properties of carbon nanotubes are governed in large extent by the functional groups present on the material, that arise from oxidation of naturally occurring defects as well as CNT oxidative purification protocols. In order to identify and quantify functional groups on CNTs, we have applied Fluorescence Labeling of Surface Species (FLOSS),[6] previously used to investigate self assembled monolayers,[6] and activated carbon fibers.[10] Carbonyl, carboxylic and alcohol groups on SWCNTs of different types (i.e. as-received, Air/HCl treated, nitric acid treated; and produced by different methods) were labeled and quantified by dyes which react with specific

Our collaborative carbon projects will use our new understanding to modify surface chemical functionality and exert chemical control on the properties of CNT. The rules we are developing on model systems (HOPG and CNT, with and without topological and functional heterogeneity) can guide the chemical modification of nanoporous carbons for a range of applications including environmental remediation and sensing.

4. Ultrafast Laser Spectroscopy of Interfaces and Development of Ultra-Broadband Pulsed Laser Sources

Ultrafast vibrational spectroscopy of water at mineral interfaces

The interaction of water with solid surfaces is of great importance to areas ranging from environmental chemistry to electrochemistry. However, it is challenging to investigate the first layer of interfacial water molecules. Vibrational Sum-Frequency Generation (VSFG) is one of the few techniques that address this challenge (Fig. 15). The mineral fluorite (CaF_2) is observed to be hydrophobic at both the macroscopic level (contact angle measurement) and microscopic (observation of free OH vibrational band). We are investigating the structure of water at CaF_2 with time and frequency domain SFG.[16] Our initial results suggest that the free OH intensity and dephasing decreases as the pH or the aqueous phase decreases from pH=13 to pH=11.

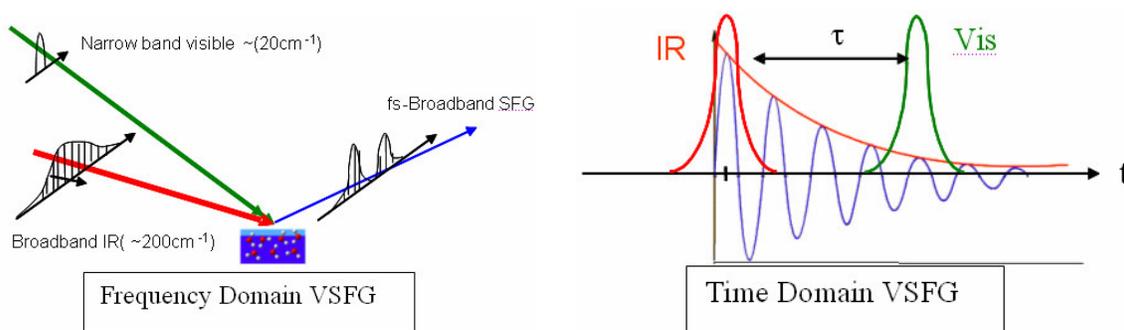


Fig. 15 Concept of Sum-Frequency Generation (SFG) Spectroscopy of interfaces. Left: SFG spectroscopy in frequency domain is performed by overlapping a broadband IR pulse and a narrowband visible pulse at the interface. Right: SFG spectroscopy in time domain wherein a short IR pulse induces coherent vibrations of oscillators at the interface which are probed with a short visible pulse delayed in time.[15-17]

Ultrafast vibrational dynamics and spectroscopy of a terminal methylene group in a siloxane self-assembled monolayer

In the past decade frequency domain Vibrational SFG spectroscopy (Fig. 15) has been applied to analyze the structure of SAMs. We are investigating the structure of SAMs by combining time- and frequency-domain SFG, namely SFG-Free Induction Decay (SFG-FID) and SFG-spectroscopy, respectively (Fig. 16). By combining these two spectroscopic techniques, we reveal the effects of UV irradiation on structure and disordering in the SAMs. The increasingly fast dephasing of the SFG-FID of C-H stretching modes with increasing UV exposure time is correlated with the appearance of methylene peaks in the SFG spectra and the appearance of defects in the SAM structure upon UV-irradiation.[15]

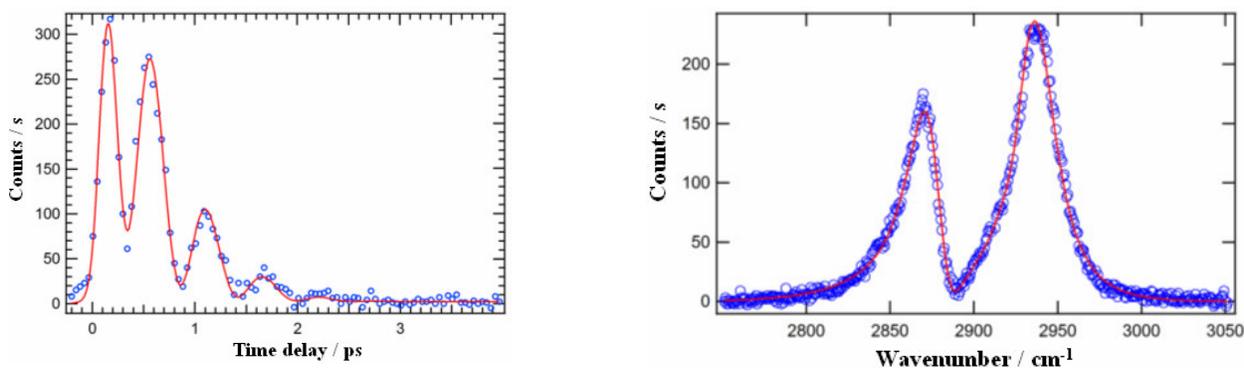


Fig. 16 SFG FID (left) and spectrum (right) of ODS SAM. The open circles represent the experimentally observed SFG signals with fit curves represented by red solid lines, respectively.[15]

Vibrational energy transfer of water at hydrophobic and hydrophilic environments

Water is ubiquitous and has great impact in environmental, biological and industrial processes. Static vibrational spectroscopy is always not sufficient enough to fully understand the role of water in those phenomena. For instance, since water constitutes $\sim 80\%$ of biological media, a number of biologically important processes depend on vibrational energy flow to and from water interfaces. Obtaining surface dynamics information requires a technique with surface specificity and selectivity.

We are performing time-resolved SFG spectroscopy in which an IR pulse, whose frequency is resonant with a vibrational mode of water, transfers population from the ground to first vibrational excited state. SFG, which acts as a probe, monitors the ground state population as a function of time after excitation by the IR pump. The recovery of SFG signal reveals the timescales of vibrational dynamics.[17] In this fashion, the subsequent vibrational energy flow in water at hydrophilic and hydrophobic interfaces can be studied in both the hydrogen bonded and free OH region.[17]

We studied the IR Pump-SFG probe dynamics of the water/silica interface in two spectral regions of hydrogen bonded water, namely 3200 and 3450 cm^{-1} , in one color setup where IR pump and IR probe had the same frequency. Our results suggest that the vibrational relaxation of hydrogen-bonded OH at the water/fused silica interface becomes faster as the bulk pH, and thus surface charge density, increases. The vibrational lifetime of O-H stretching of interfacial water in the 3200 and 3450 cm^{-1} regions at pH ~ 12 is about 200 fs , at least a factor 2 times shorter than at pH 2.[17]

Generation of ultrabroadband infrared pulses

Ultrabroad ultrashort IR sources are needed for broadband ultrafast spectroscopy, emerging field of high-order harmonic generation, remote sensing and other applications. We have developed an IR source providing $> 2500\text{ cm}^{-1}$ of bandwidth in the near-IR wavelength region (Fig. 17), and shown pulse compression to $< 40\text{ fs}$ (Fig. 18).[18, 19] This broadband pulse generation is achieved by applying the principles of non-collinear optical parametric amplification (NOPA) in potassium-titanyl phosphate (KTP) pumped at 800 nm .

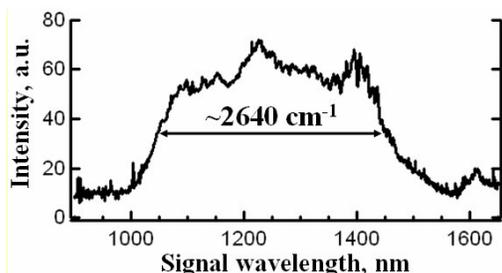


Fig. 17 Typical spectrum of the full-bandwidth NIR-signal derived from SH-spectrum of the signal off ZnSe-surface. We relate feature at ~ 1600 nm to imperfect filtering of 800-nm seed component.[18, 19]

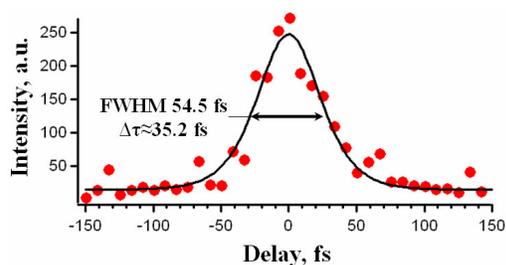


Fig. 18 Autocorrelation of signal in 30- μ m-BBO crystal (FWHM 54.5 fs, sech^2 -pulsewidth ~ 35 fs; TL ~ 8.5 fs).[18]

We have also demonstrated generation of mid-IR pulses with bandwidths >1500 cm^{-1} (Fig. 19).[20] These pulses are being applied to ultra-broadband Sum-Frequency Generation spectroscopy of aqueous interfaces. Because of the bandwidth limitations of (conventional) collinear optical parametric amplification, currently the term “broadband SFG spectroscopy” is used to describe studies in which bandwidth of IR pulse is ~ 200 cm^{-1} . With the ultra-broadband pulses from KTP-NOPA described here, it is possible to vibrationally excite different interfacial species over much wider frequency range with a single IR pulse, thus in many cases eliminating the need to tune the IR laser.

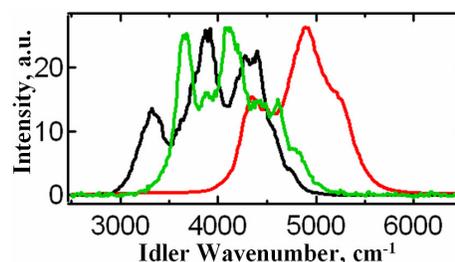


Fig. 19 Spectra of ultra-broadband mid-IR idler pulses from our KTP-based non-collinear optical parametric amplifier.[20]

Summary: Our research is discovering rules that determine structure, dynamics and reactivity at interfaces. We are using this knowledge to devise new chemical strategies to control behavior relevant to nanotechnological applications;

- Molecular engineering and self assembly at surfaces.
- Ultrathin organic and inorganic dielectrics for nanoscale devices and molecular electronics.
- Control of properties of nanoporous carbons.

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