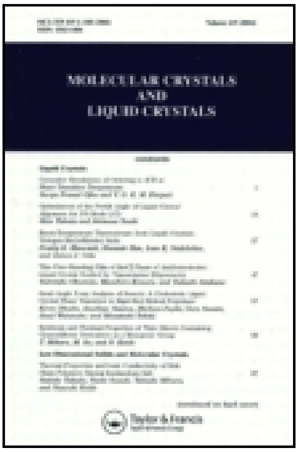

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In Situ Picosecond Studies of Surface Reaction Dynamics at GaAs (100) Interfaces

L. A. Gomez-jahn [a], L. Min [a] & R. J. Dwayne Miller [a]

[a] Department of Chemistry and Institute of Optics University of Rochester, Rochester, N. Y., 14627

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IN SITU PICOSECOND STUDIES OF SURFACE REACTION DYNAMICS AT GaAs(100) INTERFACES

L. A. Gomez-Jahn, L. Min, and R. J. Dwayne Miller
Department of Chemistry and Institute of Optics
University of Rochester,
Rochester, N. Y. 14627.

Abstract The surface restricted transient grating technique has been used to study charge transfer processes at a n-GaAs/K_2Se liquid junction. The in-situ study of interfacial hole transfer to Se^{-2} ions in solution found the hole transfer time to be less than 30 ps. Relative to the thermalization time scale of space charge accelerated hole carriers and the very efficient nature of surface state trapping, this result demonstrates that a significant fraction of the charge transfer events must involve hot hole carriers. The vertical surface transport of the photogenerated charge carriers has been characterized by a novel extension of electro-optic sampling methods to surface space charge fields.

Keywords: Surface dynamics, n-GaAs, interfaces

1. INTRODUCTION

Electron transfer across a metal or semiconductor interface to a molecular acceptor is one of the most important classes of reaction processes involved in surface chemistry. The exact mechanism of electron transfer depends on the extent of wavefunction overlap between an extended electronic state within the solid state half space and a localized molecular electronic state across the interface. The dynamics of this process are further influenced by the energetics and lattice relaxation processes involved in stabilizing charge separation, i.e., dielectric relaxation. These latter processes and the changes in nuclear coordinates associated with them affect the rate at which the system crosses the activation barrier between the reactant and product channel. This heterogeneous electron transfer process is distinct from homogeneous electron transfer in solution in that one of the electronic states is highly extended. In addition, the periodic atomic structure of the surface strongly perturbs the molecular ordering at the surface which in turn affects the electronic coupling and dielectric relaxation at the interface. Theoretical treatments of this problem have been successful in predicting qualitative features,[1] yet are limited by certain assumptions regarding the energetics and dynamics of the interface.

Direct experimental studies of the electronic coupling at the interface are needed to further refine theoretical models of surface mediated electron transfer. One approach to this problem, which is emphasized here, is to use time domain techniques to measure the electron or hole carrier interfacial transfer or surface state trapping times at a semiconductor interface. The first studies along these lines were based on fluorescence quenching.[2] However, this approach is somewhat limited in intrinsic time resolution. Herein, we describe the use of Surface Restricted Transient Grating Spectroscopy to the study of carrier reaction dynamics at semiconductor interfaces. This technique is capable of 100 fsec resolution with sub-monolayer sensitivity.[3] Specifically, the study concentrates on the dynamics of the minority carrier population (hole carrier) in a n-GaAs/K_2Se (K_2Se_2, 1M KOH) liquid junction. In addition, Surface Space Charge Electro-Optic Sampling is used to directly characterize the 100 fsec dynamics of carrier transport to within tunneling distances of the reactive surface layer.

2. EXPERIMENTAL

The grating excitation pulse sequence is shown in the inset to Fig. 1. The grating was encoded in the (100) surface of single crystals of GaAs using two above band gap excitation pulses at 532 nm. The amplitude of the grating was probed at variable time delays using below gap pulses at 1.064 μm. The experiment was conducted with a C.W. pumped, modelocked and Q-switched, YAG laser operating at 600 Hz. Single, 100 psec, pulses were selected from the Q-switched pulse train using a microwave triode based high voltage switch out. The electronic timing was accomplished with a tunnel diode discriminator that decreased the amplitude fluctuations to less than 0.5%. The 1.064 μm single pulses were frequency doubled with a β-BBO crystal and spectrally separated by a prism. The above band gap 532 nm single pulses were sent to a variable delay line and split in two with a 50% beamsplitter. The 532 nm pulses were focused and crossed at an angle at the n-GaAs surface to write the surface grating. The excitation angles were varied from 1.1^0 to 4.9^0 to measure the ambipolar carrier diffusion constant at different excitation levels. The below band gap probe pulses (1.064μm) were focused and crossed at a small angle to the excitation at the GaAs surface. The diffracted signal was detected by a large area photodiode, and sent to a lock-in amplifier interfaced to a computer. Single shot excitation conditions were varied from 6×10^{11} to 2×10^{15} photons/cm^2.

The GaAs(100) crystals (Crystal Specialties) were n-type doped with Si and both surfaces were optically polished to $\lambda/10$. The carrier doping levels were varied from $1 \times 10^{16}/\mathrm{cm}^3$ to $4 \times 10^{18}/\mathrm{cm}^3$. The doping levels were determined by electrochemical Mott-Schottky measurements. The surfaces were polished and etched in a bromine in methanol solution following the procedure of Aspnes et al. [4] to obtain the most abrupt interfaces and highest optical quality. This procedure gave a consistent surface. The n-GaAs/(Se^{-2}, Se_2^{-2}) aqueous liquid junctions were prepared by bubbling H_2Se, prepared in-situ, over a 3M KOH solution under a nitrogen atmosphere until proper stoichiometry was achieved. The selenium redox couple was transferred into an air tight three electrode cell with optical windows and a magnetic stirrer. The surface potential was monitored relative to a saturated calomel reference electrode and controlled by a regulated power supply. Excitation conditions were measured with the cell in place using a calibrated photodiode. The cell was translated to move only the crystal out of the beam path. This measures the incident intensity and corrects for absorption in the electrolyte. Reflection losses off the crystal were also measured.

Surface Space Charge Electro-Optic Sampling studies were conducted on n-

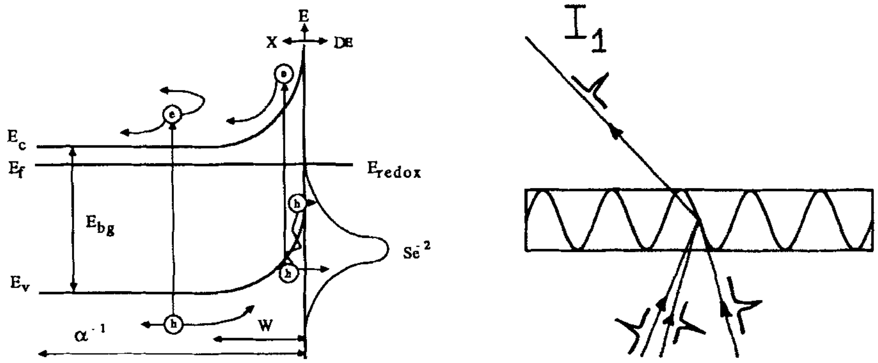

Figure 1: Photogenerated electrons and holes at the surface are separated by the space charge field with minority carriers being focused to the surface and electrons driven to the bulk. E_c, E_v, E_f, E_{bg} are the conduction and valence bands, Fermi level and energy band gap. X is the distance away from the surface of the semiconductor and D_E is the relative density of acceptor states in solution. W is the depletion layer width and α^{-1} is the optical penetration depth. Inset: Surface Restricted Transient Grating pulse sequence.

GaAs (100) oxide surfaces as a model of space charge transport. The experiments were conducted with 700 fsec pulses from a cavity dumped hybridly modelocked dye laser operating at 590 nm with an acousto-optic shutter to reduce the excitation rate to 95 KHz.[5] The dynamics of the field amplitude were sampled in reflection with the probe attenuated by more than a factor of 20- relative to the excitation. The probe angle of incidence (α) was $.1^0$ and the laser spot sizes were a 180 μm for both probe and excitation.

3. RESULTS AND DISCUSSION

3.1 In Situ Surface Restricted Grating Studies

The energetics of the n-GaAs/K_2Se liquid junction at equilibrium, in the dark is shown in Figure 1. The creation of a depletion region and an space charge field upon junction formation is of paramount importance in the present study. The photogenerated charge carriers created within the depletion layer will separate under the influence of the space charge field with the minority carrier being driven to the surface and the majority carrier driven to the bulk of the semiconductor, as shown in Fig. 1. The larger absorptivity of GaAs for above band gap excitation limit the optical penetration depth to $\alpha^{-1} \sim 1300$ Å . For typical n-GaAs conditions ($N_d = 8 \times 10^{17}$ cm^{-3}, 0.8 eV band bending), the depletion layer width is 340 Å , thus a large fraction of the photogenerated carriers are created within the space charge region. In this manner, the grating image becomes surface specific within 100 fs upon carrier generation. The minority carriers generated outside the space charge region, but within a diffusion length away, will eventually separate from the electron and be driven to the surface by the space charge field. This component to the transport

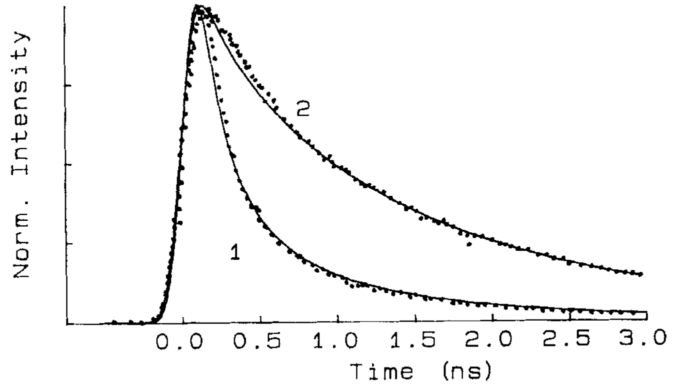

Figure 2: Surface passivation by selenide ions in solution. Curve 1: n-GaAs/air interface, curve 2: n-GaAs/selenide liquid junction at -1.50 V vs SCE. The photogenerated carrier density is 1×10^{19} cm^{-3}. The solid lines represent calculated fits using the Hoffman model. The presence of selenide ions across the interface lead to a reduction in the surface recombination velocity from 2.7×10^5 cm/sec to 3×10^4 cm/sec.

will show up as a slower diffusion limited component to the dynamics which can be easily separated on the basis of time scale from the surface image developed by the carriers initially generated in the space charge field.

The effect of selenium ion acceptors across the interface on the charge carrier dynamics can be seen in Figure 2. In this study of the GaAs interface, the space charge field due to either Fermi level pinning by the surface states or the redox couple has been completely screened by the high density of optically generated charge carriers. This has been previously confirmed by measuring the ambipolar diffusion constant under identical conditions. It was found that transport to the surface was diffusive with a diffusion constant corresponding to pure GaAs. Thus, the space charge field was screened by the high density of photogenerated carriers, i.e. near flatband conditions were obtained. As can be seen in Fig. 2, the presence of selenium ion acceptors across the interface has markedly slowed the carriers dynamics. The surface recombination velocity was obtained by fitting the grating decay using the theory developed by Hoffmann, et.al.[6] They calculated the dynamics of a free carrier grating taking into consideration the initial grating spatial profile and the surface recombination of charge carriers. The presence of selenide ions across the interface resulted in a reduction of the surface recombination velocity from 2.7×10^5 cm/sec (n-GaAs/air) to 3×10^4 cm/sec (n- GaAs/selenide). Thus, the selenium is directly affecting the surface state number density (passivation) or cross section. This results demonstrates that the selenium redox couple is in intimate contact with the surface, i.e., there is no insulating region between the acceptor ions and the surface. It is interesting to note that the grating diffraction efficiency is enhanced by a surface effect attributed to the surface states.[7]

The magnitude of an externally applied bias to the n-GaAs/K_2Se photoelectrochemical cell will determine the depletion layer width and the magnitude of the

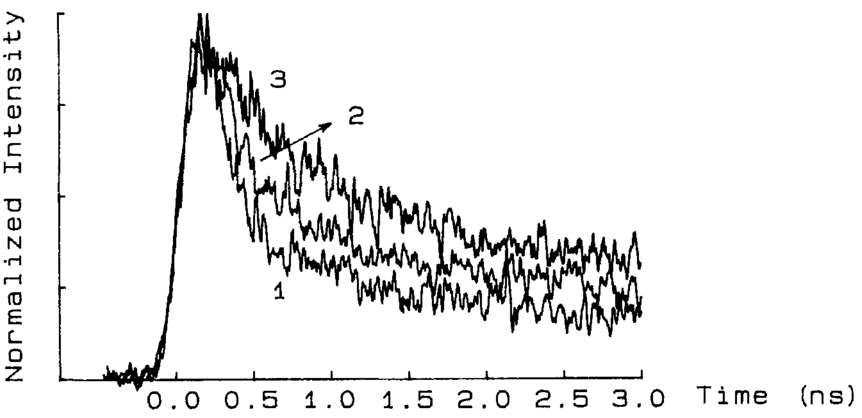

Figure 3: Carrier dynamics dependence on the applied bias for a carrier density of 1.7×10^{17} cm^{-3}. Curve 1: -1.00 V, curve 2: -1.50 V, curve 3: -1.70 V vs. SCE. For 0 V applied bias (Curve 1) field assisted transport is observed while for 0.7 V applied bias (Curve 3) ambipolar transport dominates.

space charge field. As the external bias drives the system toward flatband conditions, the depletion layer width and the space charge field are reduced. Thus, a smaller fraction of the photogenerated carriers are created within the space charge region. The effect of the reduction in the space charge field and the depletion layer width by driving the system toward flatband conditions is shown in Figure 3. The surface potential was varied from near flatband conditions to ~ 1 eV of potential drop. The flatband potential of the crystals studied were 2.1 ± .1 eV vs SCE (saturated calomel electrode) as determined by Mott–Schottky plots. For the excitation conditions used in Fig. 3, this study demonstrates that the space charge field is not significantly screened for biases corresponding to more than .6 eV of band bending (-1.5 V vs. SCE). There are two points to be made in connection to Figure 3. First, there is a marked bias dependence on the carrier dynamics. This behavior is consistent with previous observations that Fermi level pinning is significantly reduced in the presence of selenium ions across the interface.[8] Second, as the cell bias is increased, driving the system toward flatband condition, the carrier dynamics become progressively longer as a larger fraction of the carriers are generated outside the space charge region.

In order to study the influence of interfacial hole transfer on the carrier dynamics, a study of the grating signal dependence on the presence or absence of hole carrier acceptors across the interface was conducted. The results are shown in Figure 4. As can be seen in Figure 4A, in the absence on acceptors across the interface (n-GaAs/1M KOH), the signal amplitude near t=0 (peak) is significantly larger than the signal amplitude in the n-GaAs/1M K_2Se. It is important to note that the experimental conditions were identical for both systems, i.e., the same density of photocarriers were generated within the semiconductor in both cases. The concentration of K_2Se_2 was kept ≈ 1000 times lower than the concentration of K_2Se in order to minimize any surface electron transfer from complicating the dynamics. The cell was kept at -1.00 V vs SCE as higher potentials resulted in surface

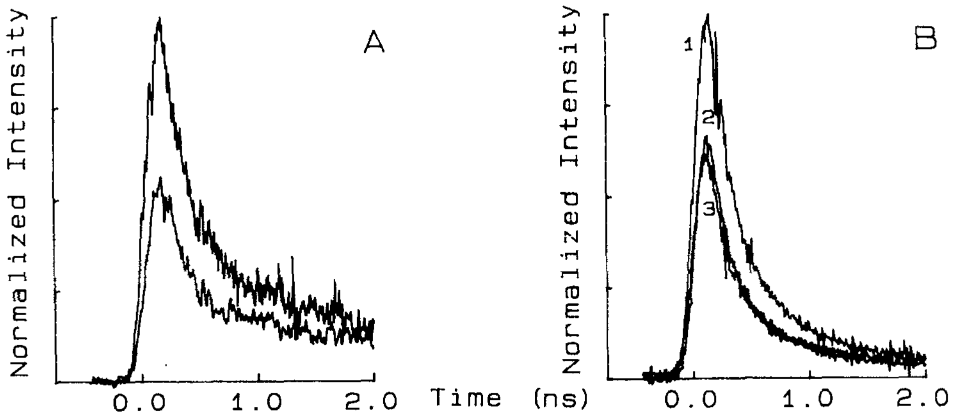

Figure 4: A: Effect of Selenide ions on grating dynamics. $N_d = 8 \times 10^{17}$ cm^{-3}. The photocarrier density is 1.7×10^{17} cm^{-3} and cell at -1.00 V vs. SCE. Top curve, n-GaAs in 1M KOH (**no acceptors**). Bottom curve, n-GaAs in 1M K_2Se (1 mM K_2Se_2, 1M KOH) under identical carrier excitation conditions. B: K_2Se concentration dependence of grating signal at 1.8×10^{18} carriers/cm^3 and -1.00 V vs. SCE. The intensities has been normalized to the highest signal at 0.21 M K_2Se. Curve 1: 0.21 M K_2Se, curve 2: 0.56 M K_2Se, curve 3: 1M K_2Se.

damage due to photo-oxidation of the GaAs surface in the absence of acceptors in solution. Also, at this electrode potential, a large fraction of the carriers ($\approx$ 30 %) is generated within the depletion layer. At the carrier density shown in Figure 4A, a substantial space charge field is present and the photogenerated electron–hole pair is effectively separated by the space charge field. The action of the space charge field and the selenium ions is to lead to selective reduction in the hole minority carrier population through surface charge transfer. The significant reduction in peak signal amplitude near t=0 also indicates that the hole transport to the surface and subsequent interfacial transfer to the selenide ions acceptors is occuring faster than our current time resolution, i.e., 30 ps. This upper limit to the hole transfer time of 30 ps illustrates the efficient nature of the hole transfer process. It is apparent that the surface is stabilized against photo-oxidation kinetically by this extremely fast hole transfer process, as assumed in earlier work.[9] The grating dynamics were also studied as a function of Se^{-2} concentration (Figure 4B). The signal amplitude is found to decrease with increasing Se^{-2} concentration which further supports the assignment of the fast grating component to hole transfer to the Se^{-2} acceptors.

The time scale for the hole transfer is also of fundamental importance in understanding electron transfer processes at surfaces. The main questions to be resolved are the electronic coupling between the molecular acceptor and band states across the interface and the effect of the density of states on the transmission probability. The upper limit of 30 psec for the hole transfer time indicates that the electronic coupling is at least on the order of a few cm^{-1}. The effect of the higher density of states on the solid state half space of the hole trajectory is expected to reduce the transmission probability, in analogy to the effect of density of states on intervalley scattering for hot electrons.[10] This aspect of the problem needs to be treated before the electronic coupling can be determined from time domain measurements of the charge transfer rate constants. In addition to this consideration, these results have some bearing on the issue of hot carrier transfer processes.

Unthermalized charge transfer processes have been implicated in non-stochastic molecular desorption from metal surfaces[11] and in solar cell devices.[12] The space charge acceleration of the hole carrier will impart approximately 1 eV of excess energy to the hole carrier which will take on the order of a picosecond to thermalize. These results suggest that even for hole transfer at least a few percent of the surface transfer processes involve hot carriers. However, better time resolution is needed to completely resolve this issue and determine the fraction of hole transfers mediated through surface states versus direct transfer.

3.2 Surface Space Charge Electro-Optic Sampling Studies (SCEOS)

The Surface Restricted Grating method takes advantage of the space charge field to field focus the minority carriers to the surface. In order to fully resolve the carrier reaction dynamics at the surface, this approch requires a clear separation in time scales between the transport to the surface and the charge transfer dynamics. The above work has demonstrated that the surface chemistry is occurring on time scales approaching the transit times of the minority carriers to the surface. This is an interesting observation which suggests that electron transfer processes are involving hot carriers potentially through strong, rather than weak, electronic coupling. However, in order to resolve completely the carrier reaction dynamics and the degree of electronic coupling an independent determination of the carrier transport is required, i.e., the transfer dynamics need to be convolved to the transport.

In order to probe this aspect of the surface chemistry, we have developed a new surface specific technique that enables a direct measurement of the carrier transport through changes in the amplitude of the surface field. This method is based on a modification of electro-optic sampling.[13] A reflected evanescent optical field is used to probe the electric field amplitude at the surface region of the semiconductor — directly at the field source rather than through a transmission line or fringe fields.[13] This approach provides the highest possible time resolution based on electro-optic sampling and makes the method surface selective.

The signal is derived from the intrinsic electro-optic effect in non-centrosymmetric semiconductors which modulates the reflectivity. The beam geometry for reflective electro-optic sampling is shown in the inset to Fig. 5. The most predominant field dependent change in the optical constants is in the indices of refraction through the linear electro-optic effect. In the present work, the space charge field is orientated along the GaAs(100) direction, i.e., in the same direction as the optical beam propagation. Thus, the field induced change in the index of refraction ellipsoid is an example of the longitudinal electro-optic effect. From the field dependence of the index of refraction and the relations for reflectivity from a birefringent surface, the reflected electro-optic signal dependence can be calculated.[5] The most important points are: 1) the signal is linearly proportional to the electric field and 2) the method has sufficient sensitivity to detect $\sim 100\ \mu$V potential changes which is adequate for surface fields of ~ 1 V.

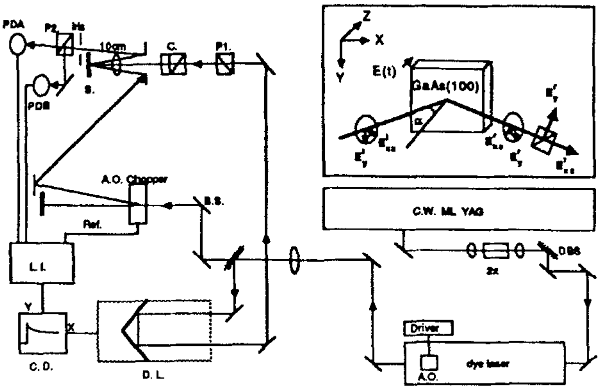

Figure 5: Experimental setup. C = babinet compensator, P = polarizer, PD = photodiode, L.I. = lock-in amp., C.D. = computer display, B.S. = beamsplitter, S = sample. The inset shows the beam geometry of the probe relative to the semiconductor surface.

This technique was used to study the sub-picosecond dynamics of electron-hole vertical transport in surface space charge fields of GaAs(100)/oxide interfaces. Space charge fields of approximately 300 Å with .8 eV potential of built in bias were generated using oxide overlayers on n-doped (3×10^{18}) (100) GaAs. The magnitude of the space charge field (2×10^5 V/cm) was measured using below band gap electro-optic sampling and optical modulation of the space charge field from full field to flat band conditions.[14] The reflective electro-optic sampling experimental setup is shown in Fig. 5. The 700 fsec pulses from the dye laser at 590 nm were used for both the excitation and the probe. In this configuration, charge carriers are optically injected within the surface space charge field by the excitation pulses. The ensuing electron-hole pair separation and transport across the space charge region causes a decrease in the space charge field amplitude. The carrier spatial transport and field amplitude can be correlated through Poisson's equation[10] such that the time dependence of the electric field transient is a direct measure of the electron and hole vertical transport.

The experimental results are shown in Fig. 6. The upper curve is the transient change in reflectivity monitored at high carrier injection ($10^{19}/cm^3$) with the reflected intensity monitored before the analyzer polarizer. This signal is proportional to the carrier population and defines the instantaneous instrument response. The lower curve is the polarization analyzed electro-optic signal at low carrier injection ($3 \times 10^{17}/cm^3$). Screening of the space charge field is less than 10% at this carrier injection level. The polarization analyzed signal was found to depend on crystal orientation as expected for the linear electro-optic effect. The range of analyzer or crystal orientations was limited by the rather small signal to noise ratio of the detected signal. However, the signal magnitude was approximately that expected from the above analysis. There is observed a small negative going coherence artifact at t = 0 for all the samples studied, in contrast to the larger positive coherence artifact observed in the transient reflectivity. The coherence artifact arises

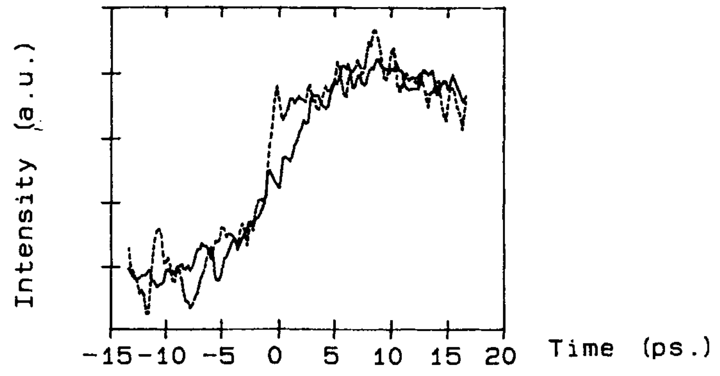

Figure 6: SCEOS signal. The upper dashed curve is the transient reflectivity at high excitation which defines the instantaneous instrument response. The lower solid curve is the polarization analyzed SCEOS signal. There is observed a small negative going coherence artifact at t = 0 (barely observable within the signal to noise in the figure) for all the samples studied, in contrast to the large positive coherence artifact observed in the transient reflectivity.

from the anisotropic polarizability of GaAs. This coherence artifact makes it difficult to deconvolve the rise time from the instrument response. However, the above results demonstrate that the rise time of the SCEOS signal is pulse width limited. Convolving different rise times to the measured pulse width has determined that the rise time of the SCEOS signal is faster than 500 fsec as a conservative lower limit.

Both the electron and the hole carrier transport contribute to the signal. The signal rise time should be biphasic with the slowest component to the signal rise time corresponding to hole carrier transport. The above results demonstrate that the hole carrier transit time across the space charge field is faster than 500 fsec. This result is expected on the basis of the mobility of the hole carrier and the space charge width. Better time resolution with shorter laser pulses will be needed to fully resolve the carrier transport over these short (100 Å) length scales. However, the above result does experimentally demonstrate that minority carrier transport to the surface, from within the space charge region, is complete on time scales shorter than carrier thermalization.

These results demonstrate the capability of SCEOS in following spatial transport over the extremely short distances and high fields present in surface space charge fields. Since the electro-optic sampling is along the field direction, there are no geometrical factors contributing to temporal broadening of the signal response function. The time resolution is limited only by the optical phonon that is coupled to the electric field driven lattice distortion. The predominant, high frequency, optical phonon mode in GaAs is 8.55 THz which gives a theoretical time resolution of ~50 fsec for this technique. Thus, this new spectroscopic method will enable a detailed determination of the carrier transport to the surface which is needed to completely decouple the charge transfer dynamics. In addition, the surface transport is occurring over length scales comparable to the carrier mean free path at fields an order of magnitude larger than that possible in the bulk. This approach should provide a rather unique probe of ballistic carrier transport.

4. CONCLUSIONS

The surface grating studies of hole capture at a liquid junction interface, with Se^{-2} as the acceptor, find a pulse width limited hole transfer component of less than 30 psec. These dynamics explain the kinetic mechanism by which selenium redox couples stabilize GaAs surfaces from photo-oxidation. However, the exact branching ratio between surface state mediated hole transfer and the direct channel from the valence band needs to be determined. With 100 fsec time resolution, it should be possible to completely resolve the surface state trapping dynamics and this branching ratio by control of the interface conditions. A detailed description of the electronic coupling between extended band states and molecular potentials at the interface depends on accurate measurements of these processes. The observed time scale for hole transfer also provides support for at least a fraction of hot carrier transfer events. The electro-optic sampling studies demonstrate the hole carriers arrive at the surface hot which further supports this hypothesis. With better time resolution (work in progress) the complete surface transport and charge transfer dynamics can be mapped out to provide a microscopic picture of the surface photochemistry and photophysics.

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