Femtosecond Laser-Induced Disorder of the (1 × 1)-Relaxed GaAs(110) Surface

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Surface physical changes (disorder and/or damage) due to femtosecond pulsed laser irradiation are observed in a new regime of extremely low laser fluence ($<10^{-3}$ of the single shot damage fluence) and large number of laser shots ($>10^{10}$). No bulk damage was detected. The surface disorder is reversible by thermal annealing at 580 °C. We propose a new mechanism for femtosecond laser-induced surface physical reactions. Disorder is caused by a surface dangling bond hole-induced lattice instability which lowers the barrier to disorder to the order of $k_B T$. This occurs during high density local fluctuations even though the mean hole density is far lower than that needed for global instability.

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Irradiation with a single ~100 mJ/cm^2 fluence femtosecond duration laser pulse can optically inject sufficient carriers into bulk semiconductors to induce a purely electronic order-disorder bulk phase transition. This has been observed in Si [1], GaAs [2], and InSb [3]. In a delocalized picture, the physics is that of the Peierl's transition: at sufficiently high carrier densities (~5% fractional occupation) the lattice is globally unstable to symmetry breaking that can lower the electronic band energy at the expense of lattice strain energy [4]. Because surface reconstruction is driven by strong surface electron-phonon interaction and a large deformation potential, we might expect the carrier density threshold for surface defect formation or phase transitions to be lower than in the bulk. Here we report the first observation of surface disorder induced by femtosecond laser irradiation. On the GaAs (110)-(1 × 1)–relaxed reconstructed surface, damage occurs at fluences that are $<10^{-3}$ of the single shot damage fluence in bulk GaAs [2]. The fractional damage yield per laser shot is $\sim 10^{-10}$, so it is possible that this damage occurs in many other systems but has not been detected. We argue here that even at low mean excitation levels, local fluctuations in electronic excitation create a temporary nonadiabatic excited state potential which allows the barrier along a particular dynamical pathway to be $\sim k_B T$. The physics is that of self-trapped-carrier defect formation: the extended carrier wave function induces a Jahn-Teller distortion when the peak local excitation density is only of order 1%.

This is a new way of thinking about nonlinear electronically induced reactions on surfaces. In most reaction kinetics, we consider the rate limited by the rare atomic fluctuations needed to overcome the ground electronic state barrier. Even in recent femtosecond laser desorption and reaction studies [5], both proposed mechanisms, multiple electronic excitations (DIMET) [6] and frictional models [7], lead to enhanced vibrational excitation and final reaction on the ground state potential. Laser-induced desorption (sputtering) of atoms from polar semiconductor surfaces including neutral Ga and P atoms from GaP [8] has been observed with ns duration pulses. Excitation of a two-hole localized surface state was proposed as the reaction transition state [9]. Recently, Tanigawa and co-workers [10] reported the desorption of Si adatoms from Si(111)-(7 × 7) with ns and fs duration pulses and proposed the same mechanism. Those experiments used fluences several orders more intense than used here and obtained yields of order 10^{-3} per shot. We believe the disorder we observe is driven by a more modest local hole fluctuation of order 2%. Similar reactions could apply whenever the carrier density can be spatially localized for a brief time, e.g., in electron and ion beam irradiation, degradation, and aging of semiconductor-device interfaces, and high energy radiation damage. Local charge fluctuations probably also play an important role in single shot damage dynamics.

In Fig. 1A we show the second-harmonic (SH) intensity measured in reflection from a (1 × 1)-relaxed GaAs (110) surface as it is irradiated continuously with a train of laser pulses at increasing pump laser fluences. The n-doped

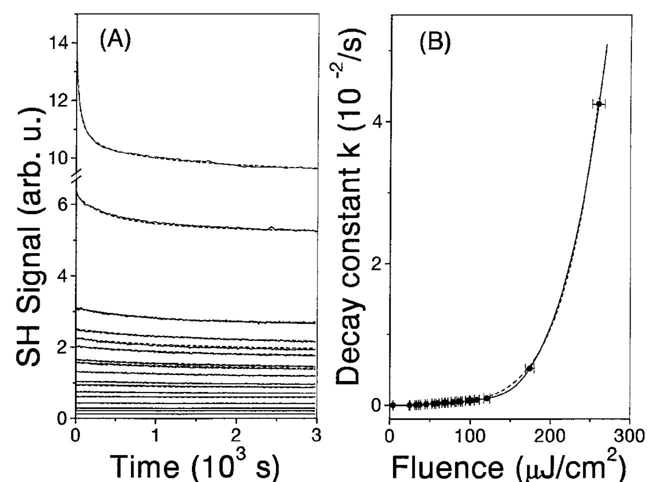

FIG. 1. (A) SH signal vs time from (1 × 1)-relaxed GaAs(110) during continuous irradiation by train of 25 fs pulses. Signals with higher amplitude obtained with higher fluence. (B) Decay rate $k(F)$ vs incident fluence/pulse obtained by the fit to data in (A). Data (solid); fit (dashed).

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(1.5×10^{18} Si/cm^3) sample was prepared in an ultrahigh vacuum chamber using alternating cycles of 400 eV Ar^+ ion sputtering and thermal annealing at 580 °C until low energy electron diffraction gave a sharp (1×1) pattern. The 25 fs duration laser pulses were obtained from a Ti:Sapphire oscillator operating at 860 nm center wavelength and 88 MHz repetition rate. The pump beam had a good fundamental Gaussian spatial profile and was focused on the sample with an achromatic lens. The radial profile in the sample focal plane was characterized by the knife-edge method and fit to a Gaussian profile with $2\omega_0 = 52\ \mu$m. The beam was incident at $\theta = 45°$, so the incident fluence was $F(x,y) = F_0 e^{-2[x^2 \cos^2(\theta) + y^2]/\omega_0^2}$. The sample was oriented so the mirror plane was lying in the incident plane. The $p_{\rm in}$-$p_{\rm out}$ surface SH generated by the pump was detected by a photomultiplier tube using color and interference filters to admit only the SH frequency and processed in a lock-in amplifier synchronized to a mechanical chopper. The SH signal was continuously corrected for laser fluence drift during a scan.

In Fig. 1A, before damage occurs the SH susceptibility $\chi^{(2)}$ is a constant and the difference in SH signal amplitudes is proportional to the square of the fluence. The decay rate clearly depends on laser fluence. We deconvolved the Gaussian spatial profile by letting the surface SH susceptibility be $\chi^{(2)}(x,y,t) = A + Be^{-k[F(x,y)]t}$, where the decay rate $k(F)$ depends on the incident fluence. The SH intensity is proportional to the square of the pump intensity, so the beam-integrated (measured) SH signal when the peak fluence is F_0 is $S(F_0,t) \propto \int_{-\infty}^{\infty} F(x,y)^2 \times |\chi^{(2)}(x,y,t)|^2\, dx\, dy \propto \int_0^{F_0} F|A + Be^{-k(F)t}|^2\, dF$. The 17 data curves are fit simultaneously (dashed lines in Fig. 1A) with good agreement using a 6th order polynomial for $k(F)$. The fit $k(F)$ is shown by a solid line in Fig. 1B with symbols marking the discrete values of F_0 used. Because $k(F)$ is so nonlinear, we use the larger 3% peak-to-peak fluence deviation from the average rather than the standard deviation as the fluence error bar. No reaction was observed in the absence of laser fluence over 10 h and our detection limit was $k(0) < 2.4 \times 10^{-6}$/s. We found no improvement for higher order polynomial fits. The rate $k(F)$ is plotted in inverse laboratory time. The fractional change in Fig. 1B per pulse is $k/(88\ \mathrm{MHz})$. The error bar for k is $<1\%$ due to each of the 17 curves containing the full $k(F)$ function for all lower fluences and the SH signal to noise being higher for higher fluence.

The SH signal decay is due entirely to a decrease in $\chi^{(2)}$ and not to changes in surface roughness or linear dielectric constants. We simultaneously measured the linear reflectivity and 30° off specular scattering and could not detect a change within our resolution of 1%. The SH signal decay is not due to enhanced conventional thermal reactions by laser heating. The average temperature rise due to laser absorption (using the diffusion equation) should be <10 K, and no change in SH is observed at such low temperatures. Finally, the SH change is not due to laser-induced surface chemical reactions with background gas species. No enhancement in SH decay rate occurred when we intentionally backfilled the chamber with O_2, H_2, or residual gas pressure with the gate valve to the vacuum pumps closed and all filaments off.

In Fig. 2, we show the coherent phonon spectra of the surface taken by time-resolved second-harmonic generation (TRSHG) [11] in a pump-probe configuration on the same spot. Figure 2A shows the evolution of the clean surface after irradiation for various times. Figure 2B shows the recovery of the phonon spectrum after the surface is initially damaged as in (Fig. 2A) and then annealed for 15 min at progressively higher temperatures. Each coherent phonon scan was obtained in 20 min with lower intensity laser beams to reduce additional damage. The surface atomic arrangement is fully recovered by annealing at 580 °C. The SH intensity also completely recovered under annealing. For the 400°, 500°, 550°, and 580° traces in Fig. 2B, the SH intensity recovered: 21.9%, 68.8%, 86.9%, and 100%, respectively, of the difference between the freshly prepared and the laser-damaged SH level.

The arrows show the center frequency for the bulk LO phonon at 8.76 THz. This feature is observed in time-resolved linear reflection spectroscopy by Kurz and coworkers and in our previous TRSHG studies of GaAs [11]. The peak at 8.76 THz initially rides on the wings of several surface phonon peaks between 7.0 and 8.5 THz [12]. After 6 h, the surface peaks are significantly reduced, and by 11.5 h, the surface features are essentially eliminated. Detailed analysis of the bulk LO phonon feature shows that it remains constant in amplitude and linewidth during the damage and annealing processes. We conclude that the disorder occurs only in the reconstructed layers of the surface. The surface phonon amplitudes decrease at about the same rate. Moreover, the temperature 580 °C required

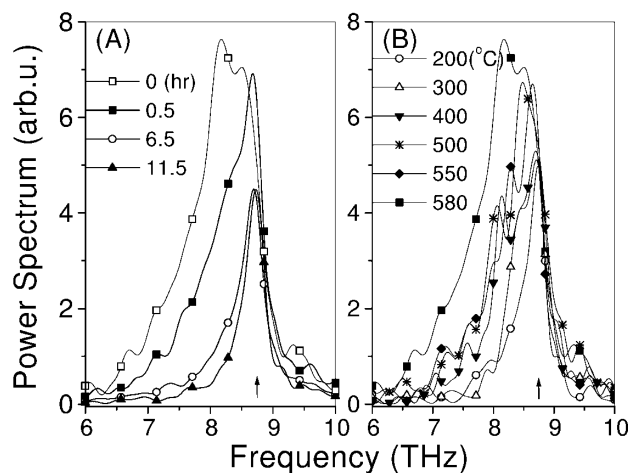

FIG. 2. (A) Surface optical phonon power spectrum during laser damage with peak incident fluence of 153 μJ/cm^2. (B) Surface optical phonon power spectrum after annealing at various temperatures. Spectra taken at 300 K to avoid artifacts due to temperature-dependent optical constants.

for annealing the laser-induced damage is the same as that required to anneal damage from Ar^+ ion sputtering. This and the proposed eigenfunctions of the surface optical phonon modes [12] are consistent with damage involving all three layers of the reconstruction and not just disorder of the topmost layer.

We compared laser-induced damage at $F_0 = 166\ \mu J/cm^2$ when the surface was clean and predosed with 100, 1100, and 6100 L [1 langmuir (L) = 10^{-6} Torr s] of molecular oxygen in the presence of a lit filament. We observed that the SH vs time fit the same kinetics as given by $k(F)$ in Fig. 1B but the SH susceptibility coefficients A and B both obeyed langmuir kinetics associated with the initial oxidation of surface dangling bond states by filament-excited oxygen at a first order rate of $(2300\ L)^{-1}$. The laser-induced disorder does not occur after dangling bond states are oxidized, even though backbond oxidation continues. We infer that excitation of the dangling bond states plays a role in the disorder mechanism.

We also compared the SH vs time for laser-pulse durations of 0.025, 0.863, 1.93, and 2.38 ps with $F_0 \sim 260\ \mu J/cm^2$. The 25 fs data are the 17th data curve in Fig. 1A. The pulse durations were stretched dispersively by passing the beam through SF10 glass. The initial SH signal decay rate was reduced by about 5 for the three longer duration pulses and we found that we could fit the four data curves using the same $k(F)$ function as in Fig. 1B but fitting an effective peak fluence F_{eff}. We found the ratio of $F_{eff}/F_0 = 1, 0.75 \pm 0.03, 0.69 \pm 0.03$, and 0.71 ± 0.03, respectively. We defined $F_{eff}/F_0 = 1$ for the shortest pulse duration, and the ratio uncertainty was dominated by the peak-to-peak fluence deviation. Since the reaction rate does not fall off exponentially to zero as a function of pulse duration, the excitation that drives the reaction must not be stored in a short-lived exponentially decaying state. We can eliminate direct optical excitation of dangling bond states due to the short lifetimes of these states. The highest lying occupied and lowest lying unoccupied dangling bond states are calculated to overlap the bulk bands at the surface Γ point and therefore should have very short lifetimes [13]. In electronic spectroscopy measurements to be reported elsewhere we found the optical coherence between these states to dephase in 10 fs at 300 K. Since scattering to the surface Γ point leads to rapid decay to the bulk, the carrier momentum dephasing time is roughly twice as long, $T_2 \sim 20$ fs. We also eliminate laser-induced coherent phonons and incoherent hot phonons excited through optical excitation of the dangling bond, because the surface phonon dephasing times are <1 ps [11], and F_{eff}/F_0 would have to be $<50\%$ in the 2.5 ps pulse case.

The only excitation with the right time scale is excitation of the highest lying normally occupied surface dangling bond hole state through coupling to the bulk hole density at the surface. Bulk holes are driven to the surface by the depletion field. The peak hole density is highest for fs laser pulses because the injected carriers can separate more rapidly and avoid bulk recombination. For ps pulses, the depletion field is reduced during the pulse and more recombination occurs before separation. This trend is well reproduced in numerical simulations of carrier dynamics [14] for 250 $\mu J/cm^2$ incident fluence as a function of pulse duration. The optical absorption in the depletion region is calculated using the absorption in nearly compensated material [15], the Franz-Keldysh effect [16], and our laser spectral distribution (810–910 nm), but ignoring transient absorption effects. Simulation details will be published separately. Time-resolved SHG studies sensitive to the depletion field recovery show the hole density at the surface relaxes on the 100 ps time scale due to bulk and surface recombination.

We also compared the SH vs time at 140 and 300 K using the same incident fluence and pulse duration (25 fs). The 300 K data are the 16th data curve in Fig. 1A with $F_0(300\ K) = 174\ \mu J/cm^3$. The reaction rate was reduced by only ~ 10 at 140 K while one would have expected $>10^{10}$ reduction for an activation barrier ~ 1 eV. The ratio between the temperature dependent optical absorption in the depletion region [15,16] at 140 and 300 K is 0.75 so the effective incident fluence $F_0(140\ K) = 130\ \mu J/cm^2$. We are able to fit the data using a fluence and temperature-dependent kinetic rate $K(F,T) \propto \nu(T)k(F)$ where the function $k(F)$ is that in Fig. 1B. The only adjustable parameters are the SH susceptibility coefficients A and B which are different at the lower temperature and the proportionality constant $\nu(140\ K)/\nu(300\ K)$ which we find to be 0.34. Using an Arrhenius relation of the form $\nu(T) = \nu_0 e^{-E_a/k_B T}$, $E_a = 25$ meV. $E_a \sim k_B T$ and much less than typical binding energies.

On the basis of the importance of exciting the dangling bond hole state and the low thermal activation barrier, we propose that the surface disorder is driven by local fluctuations in the dangling bond hole density temporarily reducing the potential energy barrier to $\sim k_B T$. This is in marked contrast to phonon-assisted electronically driven processes that have been proposed for thermally enhanced femtosecond laser-induced chemical reactions on surfaces [17]. That work suggests that the mean electronic excitation can lower barriers to reaction along selected dynamical pathways which are then accessed by the more energetic atoms in the high energy tail of the thermal distribution. Here the reaction rate $k(F)$ is dominated by the surface state hole density fluctuations.

We expect the surface reconstruction to be unstable to a high hole density in the highest lying normally occupied surface dangling bond band. Reconstruction is driven by the lowering of the dangling bond energy at the expense of lattice strain. When there are sufficient holes, the electronic energy reduction of the dangling bonds no longer compensates for the lattice strain.

Our physical picture is also quantitatively reasonable. We can estimate the mean fractional surface state hole density $\overline{n_s}$ by first assuming that the surface band density

of states is Lorentzian ($\propto[(E - E_0)^2 + (\hbar/T_2)^2]^{-1}$) with $E_0 = -0.5$ eV, e.g., 0.5 eV below the bulk valence band maximum [13], and $T_2 = 20$ fs, and second using Fermi-Dirac statistics with a Fermi level set by $E_F = -32.4$ meV $(N_b \times 10^{-19})^{2/3}$, where N_b is the bulk hole density at the surface in cm^{-3} units and is calculated as a function of fluence as described above. At 300 K with 250 μJ/cm^2 incident fluence, $N_b = 3.73 \times 10^{19}/\text{cm}^3$ and $\overline{n_s} = 0.008\,78$. Since we are primarily interested in the probability of local fluctuations $\sim 10\times$ the mean, a Poisson distribution is a reasonable choice. The dashed line in Fig. 1B is a fit of the rate $K(F,T)$ to the Poisson distribution probability that there are x excitations in an area that includes y sites ($x < y$ and are both integers) for $\overline{n_s}(F)$: $K(F,T) = \nu(T)e^{(-y\overline{n_s})}(y\overline{n_s})^x/x!$. The best fit to the curve is found when $x = 45 \pm 1$, $y = 2080 \pm 15$, and $\nu(T) = (6.21 \pm 0.25) \times 10^5$/s. Although this is a crude estimate, the fit is consistent with the rate being limited by local fractional surface hole density fluctuations of $x/y = 2.2\%$ which is the same order of magnitude as required for electronic phase transitions in the bulk. Accounting for the 88 MHz laser repetition rate, assuming the reaction occurs over 100 ps per pulse ($\sim$ restoration time of the depletion field), and using $E_a = 25$ meV, the per pulse Arrhenius rate preexponential factor $\nu_0 = 1.9 \times 10^8$ s^{-1} which is a reasonable value because it is less than surface optical phonon frequencies.

Recently, Tanimura and co-workers [10] have attributed laser-induced desorption of adatoms from the Si(111)-(7 × 7) to direct laser excitation of a localized two-hole state with a reaction rate that scales as $Y = Y_0(e^{\alpha F} - 1)^2$. This function fits $k(F)$ in Fig. 1 as well as the Poisson distribution fit. For GaAs(110)-(1 × 1), the direct photoexcited hole density is much smaller and short lived compared to the surface hole density generated by coupling to the bulk. The mean surface hole density is too low to provide much more than 2% localization with a reasonable ν_0. We cannot rule out that the disorder we see is induced by atom desorption on the basis of the loss of SH intensity or surface phonon spectra features, but it seems energetically unlikely with only a 2% hole localization. A higher and longer-lived mean surface hole density might be generated in Si if the surface hole and bulk bands overlap more favorably than in GaAs. In addition, the role of photogenerated bulk holes in surface photochemistry is well accepted, particularly in the case of adsorbate capture of a bulk hole on Si [18].

In closing, disorder of the (1 × 1)-relaxed GaAs(110) surface can be induced by ultrashort laser irradiation in the extreme multishot and low intensity regime. Disorder appears to be driven by rare, local, high density fluctuations of the surface dangling bond band holes. Since resonant laser excitation of the surface dangling bonds, hot surface holes, and hot phonons do not seem to play a role, we expect other clean or adsorbate-covered semiconductor surfaces to exhibit similar behavior whenever bulk holes accumulate near surfaces including various particle and radiation damage conditions. We gratefully acknowledge partial support under Contracts No. NSF-CHE-9707143 and No. LLNL-MRI-98-013.

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