Nonthermal transition of GaAs in ultra-intense laser radiation field

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Abstract

Using the technique of tight-binding electron–ion dynamics, we have calculated the response of crystalline GaAs when a femtosecond laser pulse excites 1–20% of the valence electrons. Above a threshold fluence, which corresponds to promotion of about 12% of the valence electrons to the conduction band, the lattice is destabilized and the band gap collapses to zero. This result supports the conclusion that structural changes on a subpicosecond time scale observed in pump-probe experiments are of a nonthermal nature.

Keywords: Laser; Phase transition; Semiconductors; Ultrafast

1. INTRODUCTION

The development of femtosecond-scale lasers, about 20 years ago, opened new research areas of ultrafast phenomena and laser-induced phase transitions. Ultrashort pulse durations, as short as 5 fs, permit a dramatic improvement in temporal resolution. Consequently, direct observation of many important phenomena became possible (Shah, 1996). In addition, a femtosecond pulse delivers an enormous amount of power, capable of disrupting practically any material by generating a small plasma of free electrons and ions. There is great potential for applications, including development of high-frequency lasers and investigation of the properties of plasmas and condensed matter under extreme conditions of temperature and pressure (Batani *et al.*, 2001).

Laser-induced transformations in semiconductor materials are of considerable practical and fundamental interest, because one would like to understand the fundamental physical processes in the newly accessible regime of short time scales and high intensities. There have consequently been a number of previous experimental observations (Saeta *et al.*, 1991; Huang *et al.*, 1998) and theoretical calculations (Silvestrelli *et al.*, 1996; Graves & Allen, 1998) of the behavior of semiconductors following ultrashort laser pulses.

Experimental observations show that the response of a semiconductor to a femtosecond-scale laser pulse (with a duration of the order of 100 fs or less) is fundamentally different than its response to a picosecond-scale laser pulse (with a duration of 1 ps or more). Whereas the longer pulses appear to produce ordinary heating of the sample by phonon emission, there is convincing evidence that ultrafast pulses induce a structural transition by directly destabilizing the atomic bonds. For example, Saeta *et al.* (1991) reported melting of GaAs after 100 fs, as evidenced by vanishing of the reflected second-harmonic signal (a signature of a symmetry change in the material). Other important experiments (Huang *et al.*, 1998; Callan *et al.*, 2000) concluded that the response of the dielectric function is dominated by changes in the electronic band structure rather than by the optical susceptibility of the excited free carriers.

Motivated by these experiments, we performed simulations of the initial stages of the laser–semiconductor interaction. We employed tight-binding electron–ion dynamics (Allen, 1994), a method applicable to general nonadiabatic processes, including the interaction with an intense radiation field. It permits simulation of the coupled dynamics of valence electrons and ionic cores in a molecule or a material. Coupling of the atomic orbitals to the external electromagnetic field is also included and, as a laser pulse is applied, valence electrons are promoted to the conduction bands.

Our model assumes a slow rate of phonon emission and does not include any electronic relaxation mechanism. Therefore, we attempt to explain the ultrafast disordering solely through destabilization of the covalent bonds by direct electronic excitation. Indeed, as a result of the laser interaction valence electrons are promoted into excited states. The en-

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ergy transfer from the "hot" photo-excited electrons to the lattice further occurs on a picosecond time scale, through a variety of carrier-lattice thermalization processes (Mazur, 1996). With ultrashort pulses, it is possible to deposit energy in the carrier system on a time scale shorter than the phonon emission time, leading to a nonequilibrium population of "hot" electrons with a still "cold" atomic lattice. If a high enough fraction of electrons are promoted from bonding to antibonding states, the crystal becomes unstable, and the structural transition occurs.

This paper is organized as follows: The key features of the molecular dynamics model are outlined in Section 2, and the main new results of our simulations are presented in Sections 3 and 4.

2. EXCITED-STATE ELECTRON–ION DYNAMICS

Standard molecular dynamics techniques assume the validity of the Born–Oppenheimer approximation. The electrons are required to follow the motion of the nuclei adiabatically, remaining in a ground-state configuration for which the one-electron states are determined by the time-independent Schrödinger equation

$$H(\mathbf{R})\Psi_j(\mathbf{r};\mathbf{R}) = \varepsilon_j(\mathbf{R})\Psi_j(\mathbf{r};\mathbf{R}). \quad (1)$$

The population of the one-electron states is thus assumed to remain invariant during the time evolution of the system. Clearly the Born–Oppenheimer approximation is not relevant to the present problem; in a system experiencing an intense laser pulse, a nonnegligible fraction of the valence electrons are promoted to excited states.

Excited-state electron–ion dynamics is a mixed quantum-classical model designed for nonadiabatic processes. As shown by Allen *et al.* (2001), two coupled equations describe the dynamics:

$$i\hbar\frac{\partial \Psi_j}{\partial t} = H(\mathbf{R},t)\Psi_j \quad (2)$$

$$M\ddot{\mathbf{R}} = -\sum_j \Psi_j^\dagger \frac{\partial H(\mathbf{R},t)}{\partial \mathbf{R}}\Psi_j - \frac{\partial U_{rep}}{\partial \mathbf{R}}. \quad (3)$$

Here H represents the usual one-electron Hamiltonian, which is explicitly time dependent when an electromagnetic field is present. U_{rep} models the repulsive forces between the ion cores. Although Ψ_j is no longer an eigenstate of the Hamiltonian, the generalized Hellmann–Feynman theorem (3) is still valid. The conjunction of the above two equations leads to a strongly interdependent picture: The electronic states determine the forces on the atoms, while the motion of the atoms (together with the applied electromagnetic field) determines the electronic states.

The electronic wavefunction is represented as a linear combination of atomic orbitals (LCAO). This approach cer-

tainly has limitations, since the LCAO basis must be kept manageable. However, this description is appropriate in the present regime of an ultrashort time scale with a moderate fraction of the valence electrons promoted to excited states.

Coupling of the electrons to an arbitrarily strong electromagnetic field is included through a time-dependent Peierls substitution. No additional parameters are required, and the applied field enters as an additional phase in the interatomic matrix elements (Graf & Vogl, 1995):

$$\mathbf{H}_{ab}(\mathbf{R}-\mathbf{R}') = \mathbf{H}_{ab}^0(\mathbf{R}-\mathbf{R}')\exp\left(-\frac{ie}{\hbar c}\mathbf{A}\cdot(\mathbf{R}-\mathbf{R}')\right), \quad (4)$$

where $\mathbf{H}_{ab}^0(\mathbf{R}-\mathbf{R}')$ represents the no-field Hamiltonian matrix element between the atomic orbitals a and b, centered on the atoms situated at $\mathbf{R}$ and $\mathbf{R}'$, respectively.

Although a first principles formulation in the LCAO basis is possible (Allen *et al.*, 2001), we find that a tight-binding representation is preferable for the present problem: (1) The electronic excitations play a central role, so it is important that the excited states be at their proper energies. (These are fitted to experiment in a semiempirical tight-binding model, whereas they are typically too low in the local density approximation and too high in Hartree–Fock.) (2) Since the time step in the simulations is of the order of 50 as, and the system may contain many atoms, the method must be computationally tractable.

The tight-binding model of Vogl *et al.* (1983) was employed here, together with Harrison's R^{-2} scaling for the interatomic matrix elements. A nonstandard repulsive potential (Graves & Allen, 1998) was used, that reproduces the experimental values of the cohesive energy, interatomic spacing, and bulk modulus—properties associated with the zeroth, first, and second derivatives of the total energy. Periodic boundary conditions were imposed on the motion of the ions, and simulations were performed in a cubical cell containing 64 atoms. With an appropriate choice for the cutoff function, the model can describe changes in bond length of up to 30% (so that the initial stages of the excitation are reliably described).

To model a laser pulse of total duration t_0, the vector potential is taken to have the time dependence

$$A(t) = A_0\cos\left(\frac{\pi(t-t_0/2)}{t_0}\right)\cos(\omega t), \quad (5)$$

where $0 \le t \le t_0$. We choose to measure the pulse strength A_0 in Gaussian units. A frequent experimental measure of pulse intensity is the fluence, commonly quoted in kilojoules per meter squared. Employing ideas from electrodynamics, one can relate the vector potential strength A_0 to the fluence F

$$F = \int_0^{t_0} S(t)\,dt = \frac{\omega^2 A_0^2 t_0}{16\pi c}, \quad (6)$$

where $S(t)$ represents the Pointing vector associated with the pulse described by Eq. (5). With $\hbar\omega = 1.95$ eV and $t_0 = 140$ fs, there results the simple connection: $F[\text{kJ/m}^2] = 0.815(A_0[\text{gauss} \cdot \text{cm}])^2$ (Graves & Allen, 1998).

The second order Eq. (3) was solved with a velocity Verlet algorithm, which preserves phase space. The first order Eq. (2) was solved with a Cayley algorithm, which conserves probability (or more generally preserves the orthonormality of the one-electron wavefunctions $\Psi_j(t)$). Further technical details on algorithms and the tight-binding model are given elsewhere (Allen *et al.*, 2001).

3. STRUCTURAL RESPONSE: DISORDERING AND LATTICE HEATING

The motivation of the present work is to determine whether lattice destabilization and bandgap collapse can be explained as a direct consequence of excitation.

A set of structural indicators are monitored during each simulation. Together, they should provide a reliable description of the laser melting process. The average atomic displacement

$$R_{avg} = \frac{1}{N} \sum_{i=1}^{N} |\mathbf{R}_i(t) - \mathbf{R}_i(0)| \qquad (7)$$

and the average kinetic energy per particle

$$K(t) = \frac{M}{2N} \sum_{i=1}^{N} \dot{\mathbf{R}}_i^2(t), \qquad (8)$$

(which is equivalent to ionic temperature) are monitored during the whole simulation after each 5-fs time interval. The pair correlation function, defined as the number of atoms within each particular distance range, is another powerful indicator which reflects very closely the laser-induced changes in the material.

The time evolution of the average atomic displacement and kinetic energy are shown in Figures 1 and 2, whereas Figure 3 shows the evolution of the average number of neighbors for two representative amplitudes of the external field. In the low intensity regime, up to $A = 1.75$ gauss·cm, the thermal lattice vibrations and kinetic energy are enhanced very little. As can be seen in Figure 3, there are no structural changes for $A = 1.5$ gauss·cm, since the distinction between first, second, and third neighbors is preserved. The curve for $A = 1.75$ gauss·cm marks the limit of the low fluency region; in spite of a large average displacement from equilibrium, the changes in kinetic energy are relatively small.

For $A = 2.0$ gauss·cm and above, the atoms are undergoing large displacements from their original positions at the same time that the kinetic energy of the atoms is increasing. The strong diffusive behavior in the R_{avg} curves is interrupted by a "knee" which appears after 200 fs. This behavior originates from the second-neighbor interaction (as we
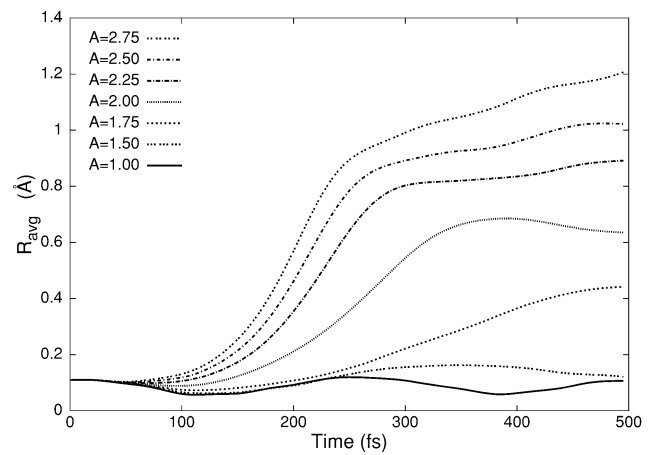

Fig. 1. Average displacement of GaAs atoms from their equilibrium positions for various intensities of the applied laser pulse. In all simulations reported here, the pulse half-width duration is 70 fs, and the full pulse extends from 0 to 140 fs. The field intensity is indicated on the upper left, with an amplitude measured in gauss·cm.

clearly observed in test runs with different cutoff values for this interaction). The fact that second-neighbor interactions become prominent is a strong signature that the crystal loses its original structure. Figure 3, showing the evolution of the number of neighbors for the case of $A = 2.25$ gauss·cm, complements this picture: The broadening of the first peak is a strong signature of a change in tetrahedral bonding, whereas the closing up of the valleys between neighbors indicates a disordered phase.

The features of the macroscopic simulations above $A = 2.0$ gauss·cm lead us to conclude that the material undergoes a structural transformation of a nonthermal nature. The behavior in these graphs clearly arises from the repulsive forces between atoms, and not from a release of the energy from excited electrons to the lattice.
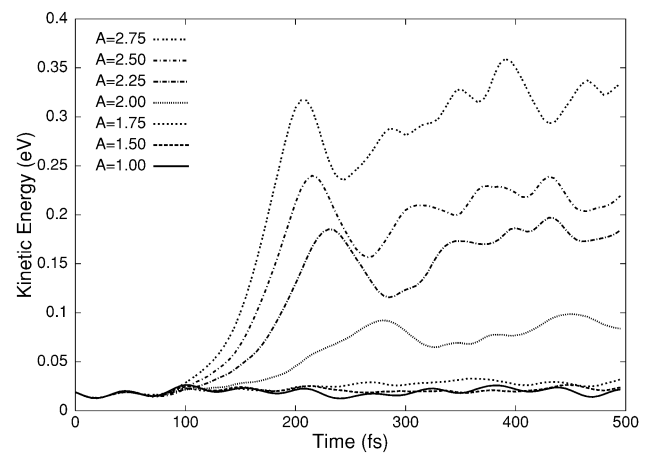

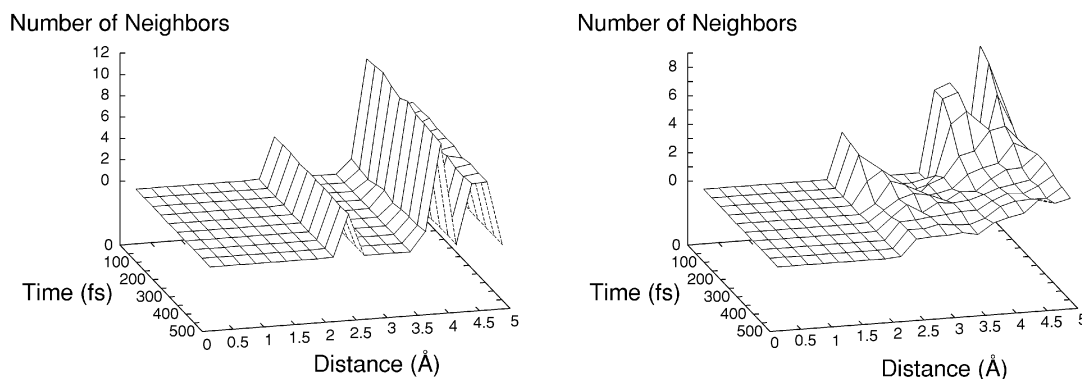**Fig. 2.** Kinetic energy of GaAs atoms for various intensities of the applied laser pulse.

Fig. 3. Time evolution of the pair correlation function for GaAs, at $A = 1.5$ gauss·cm (left), and 2.25 gauss·cm (right).

4. ELECTRONIC EXCITATION AND TIME-DEPENDENT BAND STRUCTURE

Although the wavefunction $\Psi_j(t)$ can be regarded as the physical state of electron j, it is also possible to define eigenvectors $\Phi_m(\mathbf{k})$ of the time-dependent Hamiltonian matrix:

$$\mathbf{H}(t)\Phi_m(\mathbf{k}) = \varepsilon_m(\mathbf{k})\Phi_m(\mathbf{k}). \tag{9}$$

Therefore, the occupancy of the kth state is given by

$$n_k = \sum_j |\Psi_j^\dagger \Phi_k|^2 \tag{10}$$

where $k \leftrightarrow \mathbf{k}, m$.

When an ultrashort laser pulse is applied to a semiconductor, valence electrons are promoted to the conduction bands on a time scale which is short compared to that for atomic motion ($\sim$10–100 fs vs. $\sim$100–1000 fs). The total occupancy for all the conduction bands is plotted as a function of time in Figure 4, where it is expressed as a percentage of the total number of valence electrons. One can see that the threshold value of $A = 2.0$ gauss·cm corresponds to 12% promotion of the valence electrons to conduction-band states. The effect is roughly the same as removing 24% of the bonds. There are consequently strong repulsive interactions in the initial atomic geometry, which produce massive disruption on a hundred femtosecond time scale.

An amplitude $A = 1.0$ gauss·cm corresponds to a fluence of 0.815 kJ/m^2. The threshold for permanent structural change is about 2.0 gauss·cm, or 3.26 kJ/m^2. This is about three times as large as the experimental threshold. Since the present theory yields a dielectric function roughly half that observed experimentally, one expects the nonlinear response to be underestimated also.

The eigenvalues around the band gap at the $\Gamma = (0,0,0)$ point are plotted in Figure 5 as a function of time for two different representative intensities. Notice that the band gap exhibits only thermal oscillations for $A = 1.5$ gauss·cm, and has completely closed up at $A = 2.5$ gauss·cm as a result of large atomic displacements.

The experiments of Callan *et al.* (2000) directly measure ultrafast changes in the GaAs dielectric function over the spectral range from the near-IR to the near-UV. The same quantity $\epsilon(\omega)$ can be calculated in the tight-binding approximation (Graf & Vogl, 1995; Graves & Allen, 1998).

Figure 6 shows the time evolution of Im $\epsilon(\omega)$ for the above-threshold case of $A = 2.5$ gauss·cm, when 18% of valence electrons are promoted into the conduction band. At $t = 0$, Im $\epsilon(\omega)$ is characterized by two absorption peaks E_1 and E_2. They arise from the regions in the band structure where valence and conduction bands are parallel, leading to a high joint density of states for interband transitions. As time increases, the original features are washed out, signaling the loss of the original tetrahedral bonding. Im $\epsilon(\omega)$ also becomes nonzero for photon energies below the original band gap energy of 1.4 eV, and, in fact, begins to exhibit Drude-like behavior at low energies.

The qualitative agreement with experimental data is yet more detailed: (1) The transformation starts with a sharp rise in Im $\epsilon(\omega)$ at the bottom end of the spectral range around 1.4 eV. (2) Im $\epsilon(\omega)$ shows a residual interband contribution around 3.0 eV after the semiconductor-to-metal

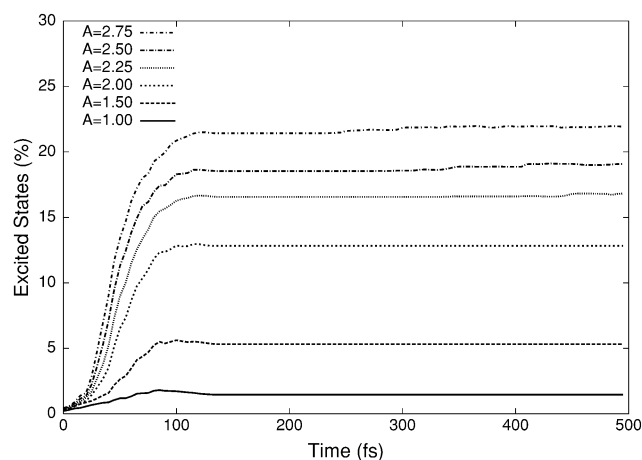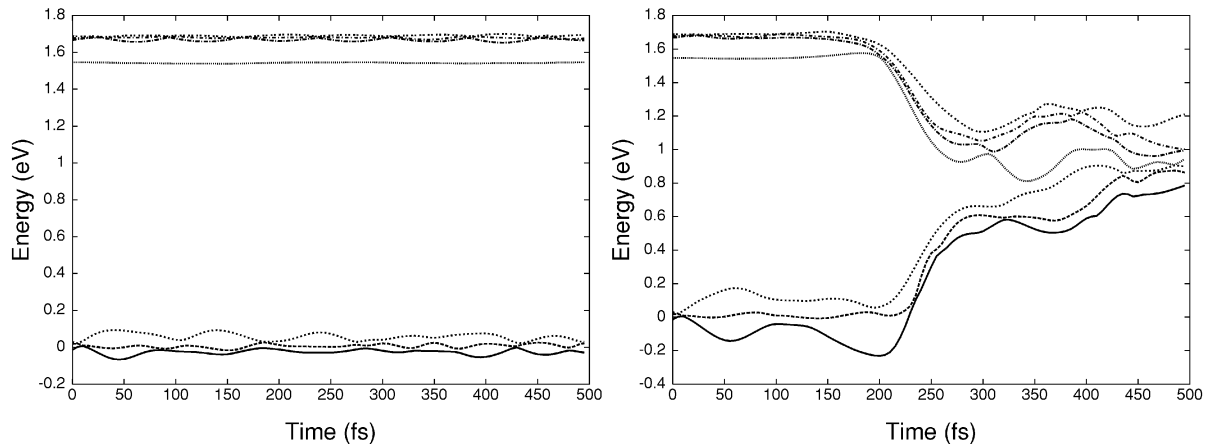**Fig. 4.** Electronic excitations for GaAs as a percentage of valence electrons.

Fig. 5. Electronic energy eigenvalues around the band gap at the Γ point as a function of time, for $A = 1.5$ gauss·cm (left) and 2.5 gauss·cm (right).

transition has occurred. Our simulation shows that this contribution originates from the states in the valence and conduction bands which originally produced the E_2 peak in unexcited GaAs, and which are much closer in energy after the band gap collapse. Therefore bonding-to-antibonding transitions occur even after the long range crystalline order is lost.

5. CONCLUSION

Using the method of tight-binding electron–ion dynamics, we have simulated the interaction of ultrashort laser pulses with GaAs. We provide a detailed microscopic picture for the coupled response of electrons and ions when an ultrashort laser pulse with a duration of 70 fs and $\hbar\omega = 1.95$ eV excites 1–20% of the valence electrons. The simulations prove that the GaAs lattice can be disrupted on a subpicosecond time scale by direct electronic excitation, when about 12% of the valence electrons are promoted to the conduction band. Accompanying the structural transformation there is a

band-gap collapse, and Im $\epsilon(\omega)$ begins to exhibits metallic behavior. The simulations presented here show good agreement with experiment in all important respects, and indicate that destabilization of the covalent bonds by direct electronic excitation is the dominant mechanism for the laser-induced phase transition.

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REFERENCES

ALLEN, R.E. (1994). Electron-ion dynamics: A technique for simulating both electronic transitions and ionic motion in molecules and materials. *Phys. Rev. B* **50**, 18629–18632.

ALLEN, R.E., DUMITRICĂ, T. & TORRALVA, B. (2001). Electronic and structural response of materials to fast, intense laser pulses. In *Ultrafast Physical Processes in Semiconductors* (Tsen, K.T., Ed.), Vol. 67, pp. 315–388. San Diego, CA: Academic Press.

BATANI, D., JOACHAIN, C.J., MARTELLUCCI, S. & CHESTER, A.N. (Eds.). (2001). *Atoms, Solids, and Plasmas in Super-Intense Laser Fields*. New York: Kluwer.

CALLAN, J.P., KIM, A.M.-T., HUANG, L. & MAZUR, E. (2000). Ultrafast electron and lattice dynamics in semiconductors at high excited carrier densities. *Chem. Phys.* **251**, 167–179.

GRAF, M. & VOGL, P. (1995). Electromagnetic fields and dielectric response in empirical tight-binding theory. *Phys. Rev. B* **51**, 4940–4949.

GRAVES, J.S. & ALLEN, R.E. (1998). Response of GaAs to fast intense laser pulses. *Phys. Rev. B* **58**, 13627–13633.

HUANG, L., CALLAN, J.P., GLEZER, E.N. & MAZUR, E. (1998). GaAs under ultrafast excitation: Response of the dielectric function. *Phys. Rev. Lett.* **80**, 185–188.

MAZUR, E. (1996). Interaction of ultrashort laser pulses with solids. In *Spectroscopy and Dynamics of Collective Excitations in Solids* (Di Bartolo, B., Ed.), pp. 417–468. New York: Plenum Press.
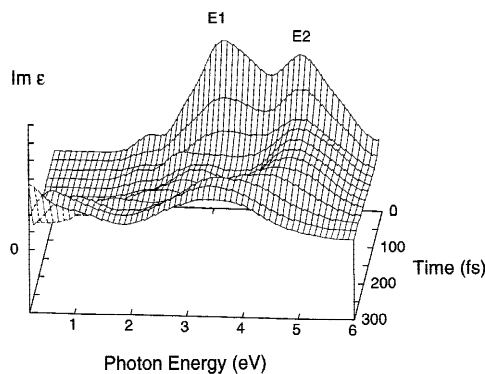

Fig. 6. Imaginary part of the time-dependent dielectric function (in arbitrary units) for an above-threshold intensity corresponding to $A = 2.5$ gauss·cm.

SAETA, P., WANG, J.K., SIEGAL, Y., BLOEMBERGEN, N. & MAZUR, E. (1991). Ultrafast electronic disordering during femtosecond laser melting of GaAs. *Phys. Rev. Lett.* **67**, 1023–1026.

SHAH, J. (1996). *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures*. Berlin: Springer.

SILVESTRELLI, P.L., ALAVI, A., PARRINELLO, M. & FRENKEL, D. (1996). *Ab initio* molecular dynamics simulation of laser melting of silicon. *Phys. Rev. Lett.* **77**, 3149–3152.

VOGL, P., HJALMARSON, H.P. & DOW, J.D. (1983). A semi-empirical tight-binding theory of the electronic-structure of semiconductors. *J. Phys. Chem. Solids* **44**, 365–378.