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Ultrashort-pulse laser heating of silicon to reduce microstructure adhesion

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Abstract—A technique to remove moisture from microelectronic devices and improve device yield in microelectromechanical systems by reducing microstructure surface adhesion is proposed. Ultrashort-pulse laser radiation is used to create excited carriers in, and consequently desorb water from, silicon microstructures. A theoretical model for ultrashort-pulse laser heating of silicon is presented. Calculated carrier temperatures show significant increases at short time scales, while the lattice temperatures remain almost constant, indicating the possibility for water desorption without significant device heating. A preliminary experiment confirming the feasibility of using the technique to decrease microstructure adhesion is discussed. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Moisture-induced device failure is a significant and persistent problem in the microelectronics industry [1]. Since incomplete moisture removal from electronic devices can lead to leakage current, oxidation and contamination [2], the removal process plays an important role in device reliability. Currently, several water removal techniques are available at the chip level, some of the conventional techniques include convection oven and vacuum bake-out processes [1].

Microelectromechanical systems (MEMS) are also subject to liquid-related problems during fabrication and operation. Sticking and the accompanying high static friction between a tiny movable part and an underlying substrate, termed *stiction*, is a major problem for microstructures and is mainly due to capillary forces from residual water [3, 4]. An example of a micromechanical device failure is shown in Fig. 1, where stiction causes the adhesion of a cantilever beam to the substrate surface. In order to avoid stiction-related device failures during fabrication, processes like sublimation and supercritical drying have been developed [5, 6]. Also, hydrophobic coatings on the silicon surfaces can be used to reduce adhesion forces due to capillary liquids on devices, as shown by Alley *et al.* [7].

This paper proposes a novel water removal technique for microelectronics and microelectromechanical systems, an ultrashort-pulse laser-induced water desorption process. The process uses ultrashort-pulse laser irradiation, with typical pulse durations on the order of or less than a few picoseconds (ps), to achieve high electron temperatures, which cause water desorption without significant increases in the lattice temperature. Thus, it is a very promising technique for use in situations where high lattice temperatures are undesirable. The process has the flexibility to remove water from large areas or selected regions down to microns [2] by changing the spot size of the laser beam. Another advantage is that the process does not require either high or low pressure.

The main emphasis of the present paper is the physical mechanisms involved in the electronic desorption process. In the following section, the physics of the process is discussed. Then, a theoretical model and numerical results for ultrashort-pulse laser heating of silicon are presented. Some preliminary experimental results are then discussed and followed by concluding remarks.

DESORPTION INDUCED BY ULTRASHORT-PULSE LASER IRRADIATION

The desorption of adsorbates from surfaces has been extensively researched [8–10], and many different mechanisms have been established. Figure 2 shows a

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NOMENCLATURE

C	heat capacity per unit volume [J $(m^3 \cdot K)^{-1}$]
E_g	band gap [eV]
g	electron (hole)–phonon coupling factor [W $(m^3 \cdot K)^{-1}$]
h	Planck's constant = 6.6262×10^{-34} [J · s]
I	laser intensity as a function of time and space [W m^{-2}]
J	laser fluence per pulse [J m^{-2}]
k_B	Boltzmann's constant = 1.38066×10^{-23} [J K^{-1}]
L	silicon layer thickness [m]
N	electron-hole pair number density [m^{-3}]
R	reflectivity
S	energy source term in the carrier energy equation [W m^{-3}]
T	temperature [K]
t	time [s]
t_p	pulse duration (full-width at half-maximum) [s]
U	energy [J]
y	spatial coordinate [m].

Greek symbols

α	absorption coefficient [m^{-1}]
α_1	one photon band-to-band absorption coefficient [m^{-1}]
σ_{fc}	free carrier absorption cross section [m^2]
γ	Auger coefficient [m^6 s^{-1}]
κ	thermal conductivity [W $(m \cdot K)^{-1}$]
λ	photon wavelength [m]
ν	photon frequency [s^{-1}]
τ_c	carrier energy relaxation time [s].

Subscripts

c	carrier (electron or hole)
l	lattice.

schematic of desorption mechanisms for water at the molecular level. Since the desorption process is a displacement of adsorbates from the solid surface, the process can be initiated by the excitation of vibrational modes between the adsorbed water and solid surface. The excitation can be realized by incident photons or by phonons in solids. In the former case, the vibrational mode is coherently excited by the incident laser. In the latter case, the solid substrate needs to be heated. Then, the phonons give energy to the surface bonds and the water molecules desorb. In these desorption mechanisms, kinetic energy of excited ion cores initiates the entire process.

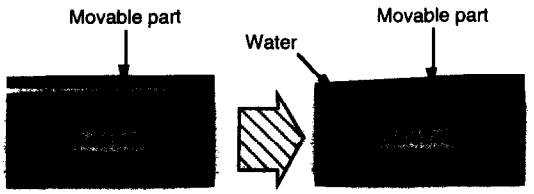

Fig. 1. Schematic of *stiction*—a major failure mechanism of microstructures.

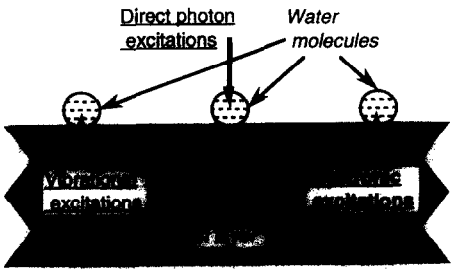

Fig. 2. Desorption mechanisms schematic.

In addition to these mechanisms, desorption can be induced by electronic excitations [9, 11]. In this case, valence or core electrons of the bonding molecules are initially excited. In this excited electronic state, the adsorbates are not necessarily in a stable state and may be either attracted to, or repulsed by, the solid surface. Consequently, the adsorbates can start moving away from the solid surface. This desorption process is different from the processes described in the previous paragraph in that it is initiated by the excited electrons or holes. Therefore, the lattice temperature of the solid is not necessarily high.

The excitation of electrons can be achieved by laser irradiation. Incident photons mainly couple with carriers in the material, which become extremely energetic. The excited carriers consist of energetic electrons in metals and electron–hole pairs in semiconductors. The energy is then transferred to the crystal lattice. The time scale for this process to begin is the energy relaxation time of carriers to phonons, which is typically 0.1 ~ 1 ps for silicon. However, if a considerable amount of energy is deposited within this ultrashort time period, the carriers will have extremely high temperatures compared to the lattice. The nonequilibrium between the carriers and lattice induced by ultrashort-pulse, high-intensity laser irradiation has been reported for metals [12] and semiconductors [13]. Qiu and Tien [14] showed that this nonequilibrium can be achieved when the laser pulse is shorter than approximately five times the electron energy relaxation time. Pulse durations of a few picoseconds or less can thus create extremely energetic carriers in silicon, and these carriers may induce the desorption of adsorbates from the surface.

Desorption induced by ultrashort-pulse laser radiation for metals and resulting electronic excitations was first reported by Prybyla *et al.* [15]. After irradiating a Pd surface with 200 femtosecond (fs), 620 nm laser pulses, they measured the desorption rate of NO molecules from the Pd surface, and showed that the total desorption yield varies superlinearly with the absorbed laser fluence. Since the desorption yield was proportional to the fluence at pulse durations longer than nanoseconds [16], a new mechanism was involved. The role of the extremely high electron temperature was later confirmed by Prybyla *et al.* [17], and a model of desorption yield was proposed by Kao *et al.* [18].

The significance of ultrashort-pulse laser desorption is that it does not require lattice heating, which can cause device damage in microelectromechanical systems. In fact, as shown in the following sections, the lattice temperature rise is practically negligible in this technique; only the carrier temperature becomes extremely high. Conventional thermal desorption processes rely on lattice heating as the desorption mechanism. Laser-induced desorption processes with longer pulse durations, in which the carriers and lattice are in equilibrium, also heat the lattice to undesirably high temperatures.

It is therefore clear from the above discussion that in order to understand the process, the carrier temperature must be determined, as desorption induced by electronic transitions depends on high carrier temperatures rather than high lattice temperatures. In the following section, a numerical model for calculating the lattice and carrier temperatures is discussed.

THEORETICAL MODEL

Figure 3 shows a schematic of the computational domain. The domain consists of a silicon layer with an adsorbed water layer either on the front or rear surface. The front surface denotes the surface that is irradiated by the laser pulse. In microelectronic applications, the silicon layer corresponds to the silicon chip, and water is adsorbed on the front surface. In micromechanical structures with stiction damage, the silicon layer corresponds to the moveable part, and the water is thus adsorbed on the rear surface of the layer.

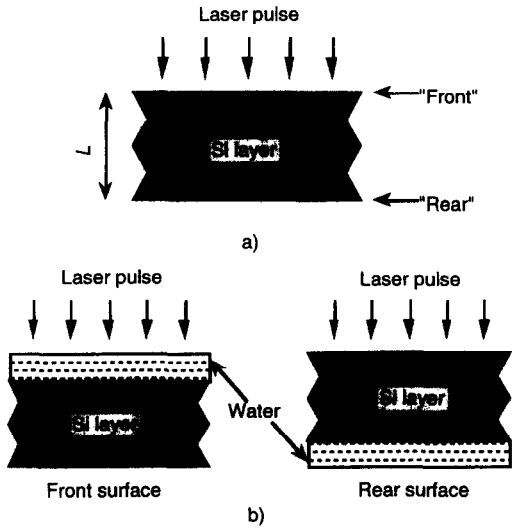

Fig. 3. Schematic of the computational domain: (a) computational domain; and (b) water adsorption on silicon surface.

As mentioned before, ultrashort-pulse laser heating of metals and semiconductors is found to raise the carrier temperature to significantly higher levels than the lattice temperature [12, 13]. Consequently, the theoretical modeling of the phenomenon needs to consider the nonequilibrium nature of the carriers and the lattice. Note, however, that in semiconductors the creation of electron–hole pairs plays a significant role in the absorption of photons [19] when the energy of incident photons is higher than the gap, E_g. Although this absorption mechanism implies a nonequilibrium between the electrons and holes, it is suggested [13, 20] that they can be well described by a single temperature, T_c. The subscript 'c' denotes the carriers, in this case, the electrons and holes.

The governing energy equations developed by van Driel [13] are employed here and given below in one-dimensional form

$$\frac{\partial U_c}{\partial t} = \frac{\partial}{\partial y}\left(\kappa_c \frac{\partial T_c}{\partial y}\right) - g(T_c - T_l) + S \tag{1}$$

$$\frac{\partial U_l}{\partial t} = \frac{\partial}{\partial y}\left(\kappa_l \frac{\partial T_l}{\partial y}\right) + g(T_c - T_l) \tag{2}$$

where t is the time, κ is the thermal conductivity, T is the temperature, and the subscripts c and l denote the carriers and the lattice, respectively. In this paper, the nonequilibrium between the optical and acoustic phonons [21] is not considered. The internal energies of the carriers, U_c, and the lattice, U_l, are defined as

$$U_c = NE_g + C_c T_c \tag{3}$$

$$U_l = C_l T_l \tag{4}$$

where N is the number density of the electron–hole pairs and C_c and C_l are the heat capacity per unit volume of carriers and the lattice, respectively. Following Agassi [20], the coupling factor, g, and the source term, S, are defined as follows:

$$g = \frac{3Nk_B}{\tau_c} \tag{5}$$

$$S = \alpha I \tag{6}$$

$$I = \frac{2\sqrt{\ln 2}J}{\sqrt{\pi}t_p}(1-R)\exp\left(-\int_0^y \alpha\, d\eta\right) \cdot \exp\left\{-4\ln 2\left(\frac{t}{t_p}\right)^2\right\} \tag{7}$$

where k_B is the Boltzmann constant, τ_c is the energy relaxation time of the carriers, α is the absorption coefficient, I is the intensity as a function of time and space, J is the laser fluence per pulse, R is the reflectivity, and t_p is the pulse duration. A Gaussian shape is assumed for the temporal profile of the intensity. The energy relaxation time of the carriers is one of the major parameters in the calculations and has a non-negligible dependency on the carrier number density [20]. The expression employed by Agassi [20] includes this dependency; however, it contains a key parameter, τ_o, that was concluded to be between 0.4 ps and 1 ps. Following van Driel's [13] constant value, τ_o is equal to 0.5 ps in the present calculations.

The carrier density of electron–hole pairs, N, is determined from the following expression:

$$\frac{\partial N}{\partial t} = \frac{\alpha_1 I}{h\nu} - \gamma N^3 \tag{8}$$

where α_1 is the one-photon band-to-band absorption coefficient, h is Planck's constant, ν is the photon frequency, and γ is the Auger coefficient. The first term in the right hand side of equation (8) represents the creation of electron–hole pairs due to the one-photon absorption process. The second term gives the loss of the electron–hole pairs through the Auger recombination process in which the free electrons are captured by ionized donors and lose their energy non-radiatively [19]. The physical properties used in the calculations are listed in Table 1.

The initial time of all the calculations is set to be $t = -5t_p$. At this time, the source term in equation (1) is negligibly small compared to its peak value. As an initial condition, a uniform carrier and lattice temperature, T_o, and a uniform carrier density of the electron–hole pairs are specified. Boundary conditions are required for the carrier and the lattice temperatures, and zero temperature gradients are used at both $y = 0$ and $y = L$ surfaces [14].

The finite difference method is employed to solve equations (1), (2) and (8) numerically. A control volume approach and the fully implicit scheme described in Patankar [23] are used for the spatial and temporal discretization schemes, respectively. A time step, Δt, of 2×10^{-15} s and a mesh size, Δy, of 5×10^{-9} m are used in the computations. Both Δt and Δy are varied before the calculations so that the calculated results are independent of the values.

NUMERICAL RESULTS

Sample calculations of the front and rear surface temperatures of a silicon layer were conducted. The laser wavelength and pulse width were 790 nm and 150 fs, respectively. The laser fluence was 3.82 mJ cm^{-2}. An undoped silicon layer with a thickness of 2.0 μm was assumed. These values are based on the preliminary experiments on device recoverability of cantilevers stuck to a silicon surface.

Figure 4 shows the temporal profile of the calculated carrier and lattice temperatures at the front and the rear surfaces. The horizontal axis represents the delay time, and the pulse peaks at $t = 0$ ps. Although the peak value of the carrier temperature reaches about 1600 K, the lattice temperature rise is extremely small (less than 2 K). These results can be

Table 1. Physical properties used in the numerical calculations

Physical property	Expression
Heat capacity of the carriers per unit volume: C_c (J(m^3-K)$^{-1}$)[a]	$C_c = 3Nk_B$
Heat capacity of the lattice per unit volume: C_l (J/(m^3-K))[a]	$C_l = 2.07 \times 10^6$
Thermal conductivity of the carriers: κ_c (W (m-K)$^{-1}$)[a]	$\kappa_c = -0.556 + 7.13 \times 10^{-3} \cdot T_c$
Thermal conductivity of the lattice: κ_l (W (m-K)$^{-1}$)[b]	$\kappa_l = 1.585 \times 10^5 \cdot T_l^{-1.23}$
Energy relaxation time of the carriers: τ_c (s)[a,b]	$\tau = \tau_o\{1 + (N/N_{cr})^2\}$ $\tau_o = 0.5 \times 10^{-12}$ (s) $N_{cr} = 2 \times 10^{27}$ (m^{-3})
Absorption coefficient: α (m^{-1})[c]	$\alpha = \alpha_1 + \sigma_{fc}N$
One-photon band-to-band absorption coefficient: α_1 (m^{-1})[c]	$\alpha_1 = 2.5 \times 10^5 \exp\{2.48(x_2 - 1.79)\}$ $x_2 = h\nu + E_g(300(K)) - E_g(T_l(K))$ (eV)
Free carrier absorption cross section: σ_{fc} (m^2)[c]	$\sigma_{fc} = 5.1 \times 10^{-22}\{1.17/(h\nu)\}^2 x_1$ $x_1 = T_l/300$ $h\nu$ (eV)
Auger recombination coefficient: γ (m^6/s)[b]	$\gamma = 3.8 \times 10^{-43}$
Reflectivity: R[a]	$R = 0.32$
Band gap: E_g (eV)[c]	$E_g(T_l) = 1.167 - 0.0258x_1 - 0.0198x_1^2$ $x_1 = T_l/300$

References: [a]Agassi [20], [b]van Driel [13] and [c]Meyer *et al.* [22].

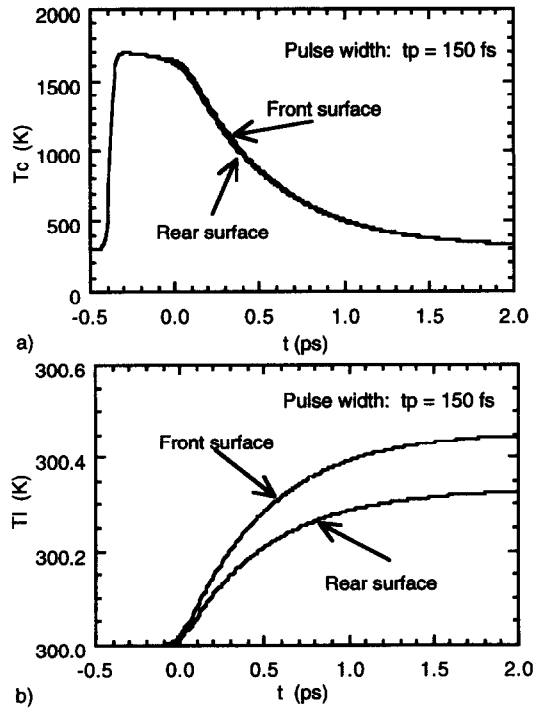

Fig. 4. Calculated carrier and lattice temperatures at the silicon layer front and rear surfaces (t_p = 150 fs, λ = 790 nm, J = 3.82 mJ cm^{-2}): (a) carrier temperature, T_c; and (b) lattice temperature, T_l.

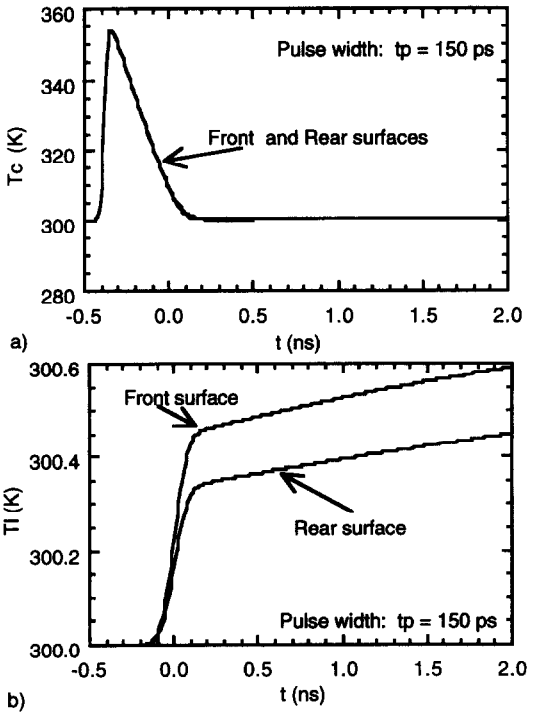

Fig. 5. Calculated carrier and lattice temperatures at the silicon layer front and rear surfaces (t_p = 150 ps, λ = 790 nm, J = 3.82 mJ cm^{-2}): (a) carrier temperature, T_c; and (b) lattice temperature, T_l.

explained by the short pulse duration compared with the carrier energy relaxation time and the small heat capacity of the carriers compared with the lattice. The former contributes to the nonequilibrium between the carriers and the lattice, and the latter realizes the extremely high carrier temperature. The extremely high carrier temperature due to the ultrashort-pulse laser irradiation suggests the possibility of water desorption induced by electronic excitations.

Figure 5 shows the calculated carrier and lattice temperatures as a function of time at the front and the rear surfaces with a pulse duration of 150 ps. All parameters are equal to the values used in the previous calculation with the exception of the time step, which is $\Delta t = 2 \times 10^{-12}$ s. Although the plots exhibit the nonequilibrium between the carriers and the lattice, the overshoot of the carrier temperature is much smaller than in Fig. 4(a). It is therefore expected that the desorption yield would be much smaller at longer pulse durations. The lattice temperature rise is almost the same regardless of the pulse duration, since the deposited energy is equal in the two cases.

EXPERIMENTAL RESULTS

Since the numerical results indicate high carrier temperatures and possible water desorption for silicon layers exposed to ultrashort-pulse laser radiation, a preliminary experiment was conducted to explore the feasibility of using ultrashort-pulse laser induced desorption to recover stiction-damaged micromechanical structures. Breaking the bonds between the rear surface of a micromachined cantilever and the remaining water beneath it lessens the adhesion forces holding the cantilever to the surface. Thus, in order to demonstrate the feasibility of using this technique to increase microelectromechanical device yield, experiments were performed and are described in ref. [24].

A preliminary experiment used a 800-nm-wavelength Ti : Sapphire laser [24]. The pulse duration and repetition rate were 150 fs and 1 kHz, respectively. The laser energy was 0.75 mJ per pulse, and the diameter of the laser beam spot was 5 mm. A stiction test structure was fabricated on an undoped silicon substrate consisting of polysilicon cantilevers ranging in length from 60 μm to 1 mm at 20 μm increments. All the cantilevers had same width (5 μm) and thickness (2 μm), and the free separation between a cantilever and the substrate was 1.5 μm. After the drying process, cantilevers 100 μm or longer on the test structure were stuck to the substrate.

Before being irradiated for 5 s, only two of the cantilevers (60 and 80 μm) were not sticking to the substrate; however, two more cantilevers (100 and 120 μm) were released from the substrate due to the ultrashort-pulse laser irradiation. Thus, the feasibility of the stiction reduction technique using ultrashort-pulse laser radiation, due to the possible mechanism

of water desorption induced by electronic excitations, was demonstrated. The microstructure recovery process and ultrashort-pulse laser desorption mechanisms are the subjects of further investigations.

CONCLUSIONS

An ultrashort-pulse laser moisture removal and microstructure adhesion reduction technique is proposed and investigated. The technique is based on electronically exciting, and thereby desorbing water from, silicon surfaces. Calculated carrier temperatures reach 1600 K when irradiated with a 790 nm, 150 fs, 3.82 mJ cm^{-2} laser pulse, which suggests the potential for desorption due to electronic excitations. However, the calculated lattice temperature remains almost constant, so device damage should be minimal using this technique. For pulse widths of 150 ps, the maximum carrier temperature reduces to around 350 K, and significantly smaller desorption yields are anticipated. It is expected that laser pulses on the order of or less than a picosecond are required to create the sufficiently large carrier temperatures needed for laser-induced desorption of water from silicon.

The calculation results confirm the potential for the ultrashort-pulse laser-induced desorption process as a means of moisture removal and stiction recovery in microelectronics and MEMS applications. A preliminary experiment further exhibited the feasibility for reducing microstructure adhesion using the proposed method.

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REFERENCES

1. W. C. Shumay, Corrosion in electronics, *Adv. Mater. Processes* **132,** 73–77 (1987).
2. C. S. Leech, Removing moisture from electronic components and assemblies, *Circuit Assembly* **5,** 34–37 (1994).
3. R. L. Alley, G. J. Cuan, R. T. Howe and K. Komvopoulos, The effect of release-etch processing on surface microstructure stiction, In *Technical Digest, IEEE Solid-State Sensor and Actuator Workshop*, pp. 202–207. Institute of Electrical and Electronics Engineers, New York (1992).
4. R. Legtenberg, H. A. C. Tilmans, J. Elders and M. Elwenspoek, Stiction of surface micromachined structures after rinsing and drying: model and investigation of adhesion mechanisms, *Sensors Actuators A* **A43,** 230–238 (1994).
5. H. Guckel, J. J. Sniegowski, T. R. Christenson and F. Raissi, The application of fine-grained, tensile polysilicon to mechanically resonant transducers, *Sensors Actuators A* **A21,** 346–351 (1990).
6. G. T. Mulhern, D. S. Soane and R. T. Howe, Supercritical carbon dioxide drying of microstructures, *Transducers '93, 7th International Conference on Solid-State Sensors and Actuators*, pp. 296–299. Institute of Electrical Engineers, Japan (1993).
7. R. L. Alley, K. Komvopoulos and R. T. Howe, Self-assembled monolayer film for enhanced imaging of rough surfaces with atomic force microscopy, *J. Appl. Phys.* **76,** 5731–5737 (1994).
8. R. Vanselow and R. F. Howe (eds.), *Chemistry and Physics of Solid Surfaces IV*. Springer, New York (1982).
9. N. H. Tolk, M. M. Traum, J. C. Tully and T. E. Madey (eds.), *Desorption Induced by Electronic Transitions DIET I*. Springer, New York (1982).
10. R. Vanselow and R. F. Howe (eds.), *Chemistry and Physics of Solid Surfaces VII*. Springer, New York (1988).
11. T. E. Madey, S. A. Joyce and J. A. Yarmoff, Desorption induced by electronic transitions. In *Chemistry and Physics of Solid Surfaces VIII* (Edited by R. Vanselow and R. F. Howe), pp. 55–68. Springer, New York (1990).
12. T. Q. Qiu and C. L. Tien, Heat transfer mechanisms during short-pulse laser heating of metals, *ASME J. Heat Transfer* **115,** 835–841 (1993).
13. H. M. van Driel, Kinetics of high-density plasmas generated in Si by 1.06- and 0.53-μm picosecond laser pulses, *Phys. Rev. B* **35,** 8166–8176 (1987).
14. T. Q. Qiu and C. L. Tien, 1994, Femtosecond laser heating of multi-layer metals—I. Analysis, *Int. J. Heat Mass Transfer* **37,** 2789–2797 (1994).
15. J. A. Prybyla, T. F. Heinz, J. A. Misewich, M. M. T. Loy and J. H. Glownia, Desorption induced by femtosecond laser pulses, *Phys. Rev. Lett.* **64,** 1537–1540 (1990).
16. F.-J. Kao, D. G. Busch, D. Gomes da Costa and W. Ho, Femtosecond versus nanosecond surface photochemistry: O_2+CO on Pt(111) at 80 K, *Phys. Rev. Lett.* **70,** 4098–4101 (1993).
17. J. A. Prybyla, H. W. K. Tom and G. D. Aumiller, Femtosecond time-resolved surface reaction: desorption of CO from Cu(111) in <325 fsec, *Phys. Rev. Lett.* **68,** 503–506 (1992).
18. F.-J. Kao, D. G. Busch, D. Cohen, D. Gomes da Costa and W. Ho, Femtosecond laser desorption of molecularly adsorbed oxygen from Pt(111), *Phys. Rev. Lett.* **71,** 2094–2097 (1993).
19. K. Seeger, *Semiconductor Physics: an Introduction* (5th Edn). Springer, New York (1991).
20. D. Agassi, Phenomenological model for picosecond-pulse laser annealing of semiconductors, *J. Appl. Phys.* **55,** 4376–4383 (1984).
21. A. Majumdar, K. Fushinobu and K. Hijikata, Effect of gate voltage on hot-electron and hot-phonon interaction and transport in a sub-micron transistor, *J. Appl. Phys.* **77,** 6686–6694 (1995).
22. J. R. Meyer, M. R. Kruer and F. J. Bartoli, Optical heating in semiconductors: laser damage in Ge, Si, InSb, and GaAs, *J. Appl. Phys.* **51,** 5513–5522 (1980).
23. S. V. Patankar, *Numerical Heat Transfer and Fluid Flow*. Hemisphere, New York (1980).
24. N. C. Tien, S. Jeong, L. M. Phinney, K. Fushinobu and J. Bokor, Surface adhesion reduction in silicon microstructures using femtosecond laser pulses, *Appl. Phys. Lett.* **68,** 197–199 (1996).