



# Matrix-assisted pulsed laser evaporation of polymeric materials: a molecular dynamics study

Tatiana E. Itina <sup>a,\*</sup>, Leonid V. Zhigilei <sup>b</sup>, Barbara J. Garrison <sup>a</sup>

<sup>a</sup> Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

<sup>b</sup> Department of Material Science and Engineering, Thornton Hall, University of Virginia, Charlottesville, VA 22903, USA

---

## Abstract

Matrix-assisted pulsed laser evaporation (MAPLE) has been recently developed to deposit high-quality thin films for a wide range of polymeric materials. To analyze the evaporation of polymer molecules in MAPLE, we present a molecular dynamics (MD) simulation of laser ablation where the target material is modeled as a solution of polymer molecules in a molecular matrix. The breathing sphere model is used for MD simulations of laser ablation of the molecular matrix. Polymer molecules are described using a bead-spring model, where each bead represents one or several polymer groups. The initial stage of polymer ejection is investigated at different laser fluences and pulse durations. The influence of polymer molecules on the stability of clusters formed in the plume and the processes that can lead to polymer decomposition are discussed. © 2001 Elsevier Science B.V. All rights reserved.

*PACS:* 79.20.D; 87.15.H; 36.40

*Keywords:* Laser ablation; Molecular dynamics simulation; Polymers; Bead-and-spring model; MALDI; MAPLE

---

## 1. Introduction

Laser ablation of molecular materials is of interest for many applications. In a number of applications, the target material is composed of a matrix of a volatile solvent with embedded large organic and biological molecules. For instance, over the past few years considerable attention has been drawn to matrix-assisted laser desorption ionization (MALDI). This technique has become one of the major methods for mass

spectrometry analysis of large fragile molecules [1]. In MALDI, large molecules are embedded into a matrix of small absorbing organic particles. Numerous experiments show that, under properly chosen experimental conditions, large molecules can survive the laser-induced volatilization.

It has been proposed recently that the processes similar to the ones in MALDI can be used for the deposition of ultra-thin and highly uniform polymer films [2,3]. The polymer films, when prepared from chemoselective materials, are used for chemical sensor development. The optimum performance of the chemical sensors depends strongly on the composition and physical properties of the

---

\* Corresponding author. Fax: +1-814-863-5319.

E-mail address: tatiana@chem.psu.edu (T.E. Itina).

polymer films. The control over the polymer composition is, thus, the critical requirement for film deposition technique. Despite the fact that pulsed laser deposition (PLD) is recognized to be an effective technique to grow thin films of materials with complex stoichiometry [2], the advantages of PLD are not so obvious in the case of polymer materials. In fact, when using classical PLD techniques for polymer targets, chemical bonds between the polymer groups are often broken. To prevent polymer decomposition under laser irradiation, a new technique called matrix-assisted pulsed laser evaporation (MAPLE) was developed [3]. The main feature of the MAPLE technique, like the one of the MALDI, is the use of a volatile molecular matrix with embedded polymer molecules as the laser target. The molecules of the matrix absorb the laser radiation and rapidly leave the surface. As a result of collisions between the matrix molecules and the embedded polymer molecules, the polymers are entrained in the plume of matrix molecules and are collected at a nearby target.

In both the MALDI and MAPLE techniques, an optimization of the experimental conditions results in the ejection of the embedded polymers intact, without chemical modifications [3]. The motion of the polymer molecules depends on both thermal and mechanical effects of the laser irradiation. To provide insight into these processes, we perform a molecular dynamics (MD) simulation study of the initial stage of molecular ejection [4,5]. Previously, the MD method was used to analyze laser desorption of guest molecules embedded into a molecular solid [6,7]. In these simulations, a detailed atomic-level description was used for organic molecules, but the sample size was small. In the present study, we use a breathing spheres model [4,5] for simulation of the laser excitation of a molecular solid, and a bead-and-spring model [8–10] for chain molecules. These coarse-grained models can allow a significant increase in the system size. The objective of this study is the investigation of the effects of laser parameters (fluence and pulse duration) on the ejection mechanisms and survivability of the polymer molecules ejected from the molecular solid.

## 2. Model

To describe the laser excitation of the molecular matrix, we use the breathing sphere model that was described in detail elsewhere [4,5]. Briefly, each matrix molecule (or group of atoms) is represented by a single particle that has the true translational degrees of freedom but an approximate internal degree of freedom. The parameters of the intermolecular potential are chosen to represent the van der Waals interaction in the molecular system. A mass of 100 amu is attributed to each matrix molecule. The parameters of a potential function ascribed to the internal motion determine the coupling between internal and translational molecular motion.

The polymer molecules are simulated using a bead-and-spring model [8]. Each bead represents a functional group of the polymer chain with mass  $m_1 = 74$  amu, which corresponds to the mass of the polydimethylsiloxane (PDMS) functional group. The chains are assumed to be flexible. Instead of the frequently used classical Rose model [9], we use a so-called hybrid model [10] that is more preferable for simulation that can involve dissociation of polymer chains. In this model, connectors (springs) show elastic (Hookean) behavior for small elongations until the spring length  $l$  reaches a certain value  $l_c$ . For elongations larger than  $l_c$ , inelastic forces of Morse types are applied. The potential energy of bonded interactions in polymers is, thus, given by

$$U_p(l) = \begin{cases} k_{\text{str}}(l - l_0)^2 - A, & l \leq l_c, \\ A[e^{-2B(l-l_0)} - 2e^{-B(l-l_0)}] \\ \quad + \Delta U_p(l_c), & l > l_c, \end{cases} \quad (1)$$

where

$$\Delta U_p(l_c) = k_{\text{str}}(l_c - l_0)^2 - A[e^{-2B(l_c-l_0)} - 2e^{-B(l_c-l_0)}]. \quad (2)$$

Here,  $l_0$  is the equilibrium spring length,  $k_{\text{str}}$  is the stretching force constant,  $A$  is the dissociation energy of the spring. The parameter  $B$  is set to be  $\sqrt{k_{\text{str}}/2A}$ . For given values of  $A$ ,  $l_0$ ,  $k_{\text{str}}$  and  $B$ , the parameter  $l_c$  can be determined if one requires that the first derivative of  $U(l)$ , i.e., the force, is con-

tinuous at  $l = l_c$ . The described model combines the desirable features of the Hookean springs at small spring elongation with dissociation behavior at large elongations.

For bonded interactions in polymers, we use the parameters typical for siloxane polymers [11] (e.g., PDMS), where  $l_0 = 1.64 \text{ \AA}$ ,  $A = 4.6 \text{ eV}$  and  $k_{\text{str}} = 8.42 \text{ eV/\AA}^2$ . The calculated parameters are  $B = 0.96 \text{ \AA}^{-1}$  and  $l_c = 1.7 \text{ \AA}$ . When the bond length exceeds  $l_c = 7.7 \text{ \AA}$ , the chemical bond will be broken leading to the polymer fragmentation. After the fragmentation, the interaction between the previously bonded beads will be calculated as the one between non-bonded beads. For non-bonded interactions in polymer molecules, as well as for polymer bead-matrix molecule interactions, we use the Morse potential with the same parameters as for interactions among the matrix molecules [4,5]. Because the coarse-grained models are used both for matrix molecules and for polymers, a fairly large time step of 2 fs is used in the simulation.

### 3. Simulation systems

The calculations are performed for two different systems. First, we use a rectangular sample with linear dimensions of  $100 \times 100 \times 900 \text{ \AA}^3$  that contains 62 577 matrix molecules. Nine polymer molecules, each composed of 40 beads are introduced into the sample unit cell using a random Monte Carlo procedure. Before exposing to a laser pulse, the system is equilibrated. Dynamic boundary conditions are used to eliminate the reflection of the laser-induced pressure wave from the bottom of the simulated sample [12]. At the cell sides, periodic boundary conditions are imposed. Laser irradiation is simulated by vibrational excitation of randomly chosen matrix molecules. The vibrational excitations are performed by depositing a quantum of energy equal to the photon energy into the kinetic energy of internal vibration of the molecules to be excited. The absorption probability decreases exponentially with depth in accordance with Beer's law. The laser penetration depth,  $L_p$ , is assumed to be  $500 \text{ \AA}$  in this system.

Two different pulse durations of  $\tau = 15 \text{ ps}$  (short pulse) and  $150 \text{ ps}$  (long pulse) at a wavelength of  $337 \text{ nm}$  are used. The laser fluence is set to be  $61 \text{ J/m}^2$ , a value well above the ablation threshold in the simulations [13,14].

The second sample is spherical with the diameter  $d = 180 \text{ \AA}$  and contains a total number of 178 427 matrix molecules and one polymer chain with 200 beads. This set of simulations is used to reproduce the processes occurring in the ablation plume at a more realistic longer length scale. Here, the laser radiation is uniformly distributed among the matrix molecules, and boundary free conditions are used. The energy density  $e = 0.6 \text{ eV}$  per molecule is used in the calculations. The value of energy density is chosen so that it corresponds to the average energy per particle in the upper layer with the width of  $290 \text{ \AA}$  at a laser fluence of  $61 \text{ J/m}^2$  in the first system.

### 4. Results and discussion

To examine the initial stage of molecular ejection as a result of laser excitation, several MD simulations are performed. First, we investigate the motion of guest polymeric molecules induced by laser excitation of the molecular matrix under the conditions of typical laser ablation experiments. The first system with nine polymer chains is used to model the conditions at the center of the laser-irradiated region. Then, we turn to the spherical system in order to reproduce in a larger scale the conditions that are found to be realized inside the ablated plume at the stage of its development.

First we present the results obtained in the case of the rectangular system. Fig. 1 visualizes the laser plume obtained at  $F = 61 \text{ J/m}^2$  for two different pulse durations ( $\tau = 15$  and  $150 \text{ ps}$ ) at  $200 \text{ ps}$  after the end of the laser pulse. One can see in the figure that as a result of the laser irradiation the matrix molecules are ejected from the surface forming the ablated plume. The plume structure is different at different pulse durations. Whereas at both pulse durations the laser irradiation results in a rapid ejection of a large number of matrix molecules and clusters, for the shorter laser pulse the

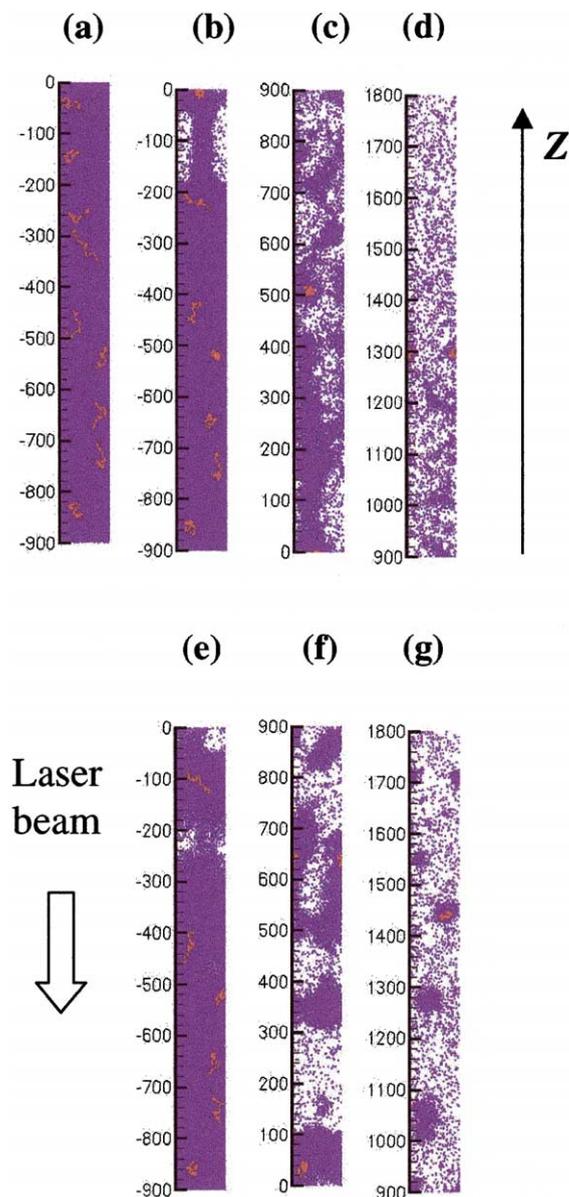


Fig. 1. Snapshots from the MD simulation obtained before the laser irradiation (a) and at 200 ps after the end of the laser pulse for two different pulse durations  $\tau = 150$  ps (b, c, d) and  $\tau = 15$  ps (e, f, g). Here, the laser fluence  $F$  is  $61 \text{ J/m}^2$ . The snapshots shown in the frames (b, c, d) as well as the ones presented in (e, f, g) display the different parts of the same laser plume in the direction normal to the surface. The Z-axis is directed along the outward surface normal, the position of the irradiated surface corresponds to  $z = 0$ . For better presentation, the polymer molecules (red) are plotted above the matrix molecules (blue), whereas in reality they are inside the sample.

yield of the ablated material is larger. In addition, for the shorter laser pulse there are more clusters ejected and they are bigger and faster [13,14]. The figure shows that the polymer molecules embedded into the molecular matrix move together with the ablated matrix material. The polymers that were initially embedded closer to the irradiated surface are found to move more rapidly than the ones that were embedded deeper.

The motion of polymer molecules that were initially embedded at different depths below the irradiated surface  $z = 0$  [initial center-of-mass positions  $z = -42, -149, -262, -314, -480 \text{ \AA}$ ] is illustrated in Fig. 2. One can see that when laser duration is shorter ( $\tau = 15$  ps), the polymer molecules that are located in the vicinity of the sample surface start moving almost immediately after the end of the laser pulse and move more rapidly than at the longer laser pulse ( $\tau = 150$  ps). The slope of the curves gives the velocities of polymer molecules. The velocities of polymer molecules are found to decrease exponentially with the initial position below the surface (Fig. 3). For  $\tau = 15$  ps, the velocity of the upper chain reaches the value as high as 750 m/s.

The differences in the plume structure and in polymer motion at different pulse durations can be explained by the fact that if the laser pulse duration is shorter than the characteristic stress propagation time,  $t_p$ , a high thermoelastic pressure build-up is induced within the sample, and the *stress confinement* regime can be realized [13,14]. For the longer laser pulse, the thermoelastic pressure is not significant. In this case, the pulse duration is longer than  $t_p$  but shorter than the time of dissipation of the absorbed energy by the thermal conduction the *thermal confinement* regime is realized.

Interestingly, the simulations at both pulse durations indicate that polymer molecules have strong tendency of being located inside the clusters of matrix molecules. This trend can be explained by the fact that matrix molecules can be attracted by two or several neighbor polymer beads. Because each of the polymer beads attracts the matrix molecules in the same way as any matrix molecule, the matrix molecules tend to stay localized in the vicinity of the polymer. Therefore, the material located around the polymer molecule is

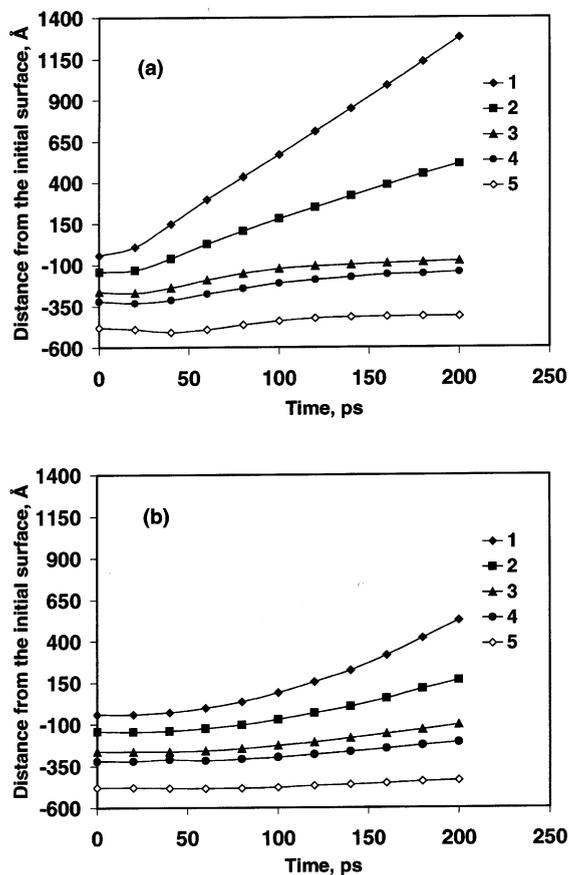


Fig. 2. Z-positions of the center-of-mass of the polymer molecules initially embedded at different depths as a function of time. (a) Simulation results for laser pulse duration  $\tau = 15$  ps and laser fluence  $F = 61$  J/m<sup>2</sup>. (b) Simulation results for laser pulse duration  $\tau = 150$  ps and laser fluence  $F = 61$  J/m<sup>2</sup>. The Z-axis is directed along outward surface normal,  $z = 0$  corresponds to the initial position of the irradiated surface.

ejected in the form of clusters. Moreover, if a polymer molecule is in the cluster, the polymer can stabilize the cluster. Being located in the clusters, polymers are not subjected to the pressure gradient and can exchange their energy with the surrounding molecules.

To imitate the conditions inside the ablated plume at the same energy density as in the simulations presented below, but to focus the attention on the behavior of a large volume containing a polymer molecule, we used the spherical sample with one long polymer chain in it. As a result of fast deposition of laser energy, the temperature of

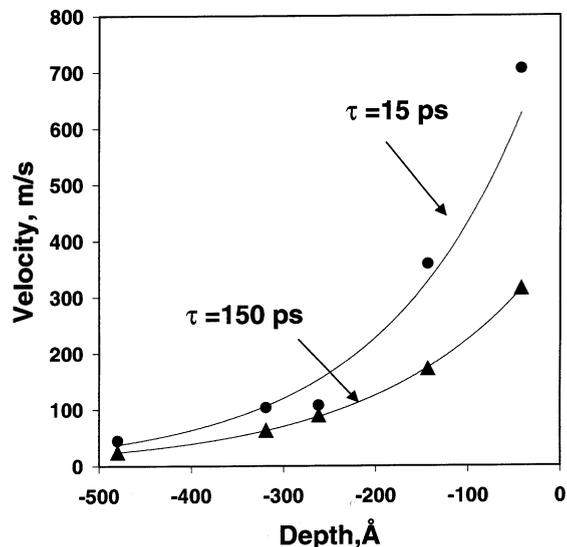


Fig. 3. Velocity of the center-of-mass of polymer chains in the direction normal to the surface as a function of the initial depth below the irradiated surface for two different laser pulse durations and laser fluence  $F = 61$  J/m<sup>2</sup>. The dependencies are fitted by exponential functions.

the material rises, and strong pressures build up in the cluster [15]. A snapshot from the simulation obtained at  $t = 300$  ps after the beginning of the laser pulse is shown in Fig. 4. The calculations are performed for energy density  $e = 0.6$  eV per molecule and pulse duration  $\tau = 15$  ps. One can see in the figure that the big cluster is decomposed into a number of smaller clusters. In addition, a large number of matrix molecules are ejected in the form of monomers. Both the monomers and the small clusters expand rapidly outward from the cluster center. The polymer molecule also moves away from the cluster center. Nevertheless, parts of polymer still remain incorporated into clusters. The movement of the clusters in the radial directions apparently strains the polymer chain, Fig. 4. Because of the strong bonded interactions, the polymer molecule is not fragmented during the ablation event.

## 5. Summary

The MD simulations show that as a result of laser excitation, polymer molecules embedded in a

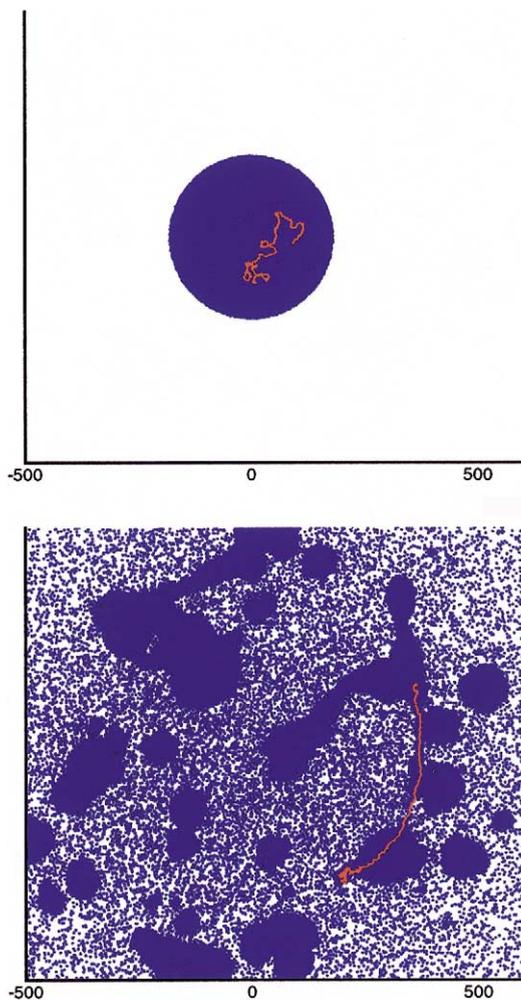


Fig. 4. A snapshot from the simulation for the spherical system obtained before the laser irradiation (a) and at  $t = 300$  ps after the beginning of the laser pulse with pulse duration  $\tau = 15$  ps. The energy density  $e = 0.6$  eV per molecule is deposited by the laser pulse. For a better presentation, the polymer molecules (red) are plotted above the matrix molecules (blue). The distances are measured in Ångstroms.

molecular matrix can be ejected together with the matrix material. Two different regimes of laser ablation, stress confinement and thermal confinement, are considered. In these regimes, the motion of the polymer molecules embedded into the matrix at different depths is followed. The polymers are found to move faster and to start moving earlier when the laser pulse is shorter. It is shown that polymer velocities in the direction normal to

the surface are not thermal and decrease exponentially with the initial depth.

The calculations show that at laser fluences above the ablation threshold, big clusters are formed in the plume. It is demonstrated that the polymer molecules in a molecular solid tend to be located inside the clusters and stabilize the clusters as the plume expands.

In addition, to reproduce the conditions realized in the developing ablated plume, a simulation of the decomposition of a laser-heated volume containing one polymer molecule is performed. As a result of the rapid pressure build-up, the volume breaks into a number of smaller clusters. At later times, parts of the polymer molecule remain incorporated in smaller clusters that continue expanding. We note that the polymer molecule is not fragmented during the ablation event. Work on more detailed investigations of the laser ejection of macromolecules embedded into a molecular solid is underway.

### Acknowledgements

This work was supported by the United States Office of Naval Research through the Medical Free Electron Laser Program and by the National Science Foundation through the Chemistry Division. The computational support was provided by IBM through the Selected University Research Program, the National Science Foundation through the MRI Program, and the Center for Academic Computing at Penn State University. The authors are thankful to Yaroslava Yingling and Gareth Williams for helpful discussions.

### References

- [1] M. Karas, in: P. Sigmund (Ed.), *Fundamental Processes in Sputtering of Atoms and Molecules*, Det Kongelige Danske Videnskabernes Selskab, Copenhagen, 1993.
- [2] D.B. Chrisey, C.K. Hubler (Eds.), *Pulsed Laser Deposition of Thin Films*, Wiley, New York, 1994.
- [3] A. Piqué, R.C.R.A. McGill, D.B. Chrisey, J. Callahan, T.E. Itina, *Mater. Res. Soc. Symp. Proc.* 526 (1998) 375.
- [4] L.V. Zhigilei, P.B.S. Kodali, B.J. Garrison, *J. Phys. Chem. B* 101 (1997) 2028.

- [5] L.V. Zhigilei, P.B.S. Kodali, B.J. Garrison, *J. Phys. Chem. B* 102 (1998) 2845.
- [6] A. Bencsura, V. Navale, M. Sadeghi, A. Vertes, *Rapid Commun. Mass Spectrosc.* 11 (1997) 679.
- [7] X. Wu, M. Sadeghi, A. Vertes, *J. Phys. Chem. B* 102 (1998) 4770.
- [8] K. Kremer, G.S. Grest, *J. Chem. Phys.* 92 (8) (1990) 5057.
- [9] H.C. Öttinger, *Stochastic Processes in Polymeric Fluids*, Springer, Berlin, 1996.
- [10] J.J. López Cascales, F.G. Díaz, J. García de la Torre, *Polymer* 36 (2) (1995) 345.
- [11] S.J. Clarson, J.A. Semlyen, *Siloxane Polymers*, PTR Prentice Hall, Englewood Cliffs, NJ, 1993.
- [12] L.V. Zhigilei, B.J. Garrison, *Mater. Res. Soc. Symp. Proc.* 538 (1999) 491.
- [13] L.V. Zhigilei, B.J. Garrison, *Appl. Phys. A* 69 (1999) S75.
- [14] L.V. Zhigilei, B.J. Garrison, *J. Appl. Phys.* 88 (2000) 1281.
- [15] L.V. Zhigilei, B.J. Garrison, *Appl. Surf. Sci.* 127–129 (1998) 142.