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MODELING AND SIMULATION OF PULSED LASER ANNEALING AND ABLATION OF SOLID MATERIALS

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ABSTRACT

A previously developed one-dimensional (1D) computational model for heat flow and nonequilibrium phase change phenomena induced by pulsed-laser irradiation has been extended to two-dimensions. The 2D modeling focuses attention on the heat flow from localized sources embedded in an otherwise planar matrix. For example, nucleation events occurring in undercooled liquids such as molten Si formed by pulsed-laser melting of amorphous Si (a-Si) and inhomogeneous absorption due to randomly occurring defects in targets used for pulsed-laser ablation can be treated. Concepts introduced in the 1D modeling, such as the state diagram and the state array are extended to 2D and refined. As an example of the calculations that are now possible, the laser-induced formation and propagation of buried liquid layers are followed in two dimensions for the case of a-Si on a crystalline silicon substrate. It is demonstrated how solid phase growth from individual nucleation sites gives rise to a nearly planar liquid layer propagating through the a-Si. Another example briefly addresses questions related to the early stages of the laser ablation of insulators such as MgO, where it is believed that the absorption of the laser radiation occurs at localized but extended regions of high concentrations of defects. The 2-D program has been rewritten for massively parallel machines such as the Intel Paragons in ORNL's Center for Computational Sciences by one of us (CLL), thus allowing larger and more accurate calculations for complex systems to be carried out in reasonable times.

I. Introduction

Materials processing with pulsed lasers has developed rapidly in recent years and has proved to be of considerable interest for both applied and fundamental fields of condensed matter physics and materials science. Initially the emphasis was on laser annealing [1], but in recent years interest in pulsed-laser ablation for thin film deposition and other applications has escalated rapidly [2]. Theoretical treatments of both the annealing and ablation processes have generally proceeded from one-dimensional models which are often entirely adequate. However, there are certain types of problems in both processes for which a 1D approach is inadequate. For example, after the laser annealing of an a-Si layer on a crystalline silicon (c-Si) substrate, transmission electron microscopy [3] reveals microstructure, suggestive of rapid outward growth from point nucleation sites, which clearly can not be explained by a purely 1D approach. In the laser ablation of insulators [4] there is considerable evidence that absorption by isolated, randomly scattered near-surface defects play an important role. Consequently, there is a need for the development of 2D models to be used in explaining such features. In previous work, a one-dimensional model and a computer program (called LASER8) were developed to deal with various pulsed-laser annealing phenomena [5,6]. Recently this program was incorporated into a larger laser ablation [7] program. In this paper, we extend this 1D approach to two dimensions.

Annealing of a-Si by pulsed lasers has been a model system for studies of a variety of phase changes under nonequilibrium conditions resulting from ultrarapid heating and cooling induced by laser pulses. One of the most interesting phenomena is that the laser pulse may produce a buried liquid layer that propagates within the a-Si. Solidification from this moving layer often results in either fine-grain or amorphous silicon. Formation and propagation of the layer is due to the unusual properties of a-Si compared to c-Si. The melting temperature of a-Si, T_a , is about 225 K lower than that of c-Si ($T_c=1685$ K) and the

thermal conductivity, K_a , is also low, with a temperature-averaged value (room temperature to T_a of 0.01-0.02 W/cm K, between one and two orders of magnitude smaller than the temperature-dependent thermal conductivity of c-Si, K_c . In addition, the latent heat of a-Si, L_a , is only about 0.73 L_c [8], where L_c is the heat of fusion of c-Si. On melting, Si becomes metallic with the reflectivity R , at $\lambda = 633$ nm increasing by 75% and the electrical conductivity by a factor of 20. Therefore, nanosecond-pulsed-laser melting of a-Si at an energy density (E_l) just above the threshold for melting results in a highly undercooled liquid whose formation and subsequent behavior can be studied directly by time-resolved electrical [9,10] and optical [11] measurements.

In the modeling underlying the LASER8 program, a state array concept was introduced which allows a wide variety of physical effects to be simulated as an adjunct to the heat flow and phase change calculations [5,6]. The state array essentially specifies a number of conditions which the material in a given finite-difference (FD) cell and its neighboring cells must satisfy in order for a phase transition and/or a change in microstructure to occur. Through the introduction of "timers" in a generalized sense these conditions may be made time-dependent. For example, it may be required that the conditions in and around a given FD cell persist for some period of time before a nucleation event can occur. In such a case, we can simulate the nucleation kinetics on a gross scale without going to the level of a molecular dynamics calculation.

II. Two-dimensional modeling of pulsed-laser interactions with solid materials

In the version of the 2D program to be described here, the sample is divided into a collection of contiguous semi-infinite hexagons as in Fig.1a. The idea is that some event will occur at the center of each hexagon more or less simultaneously across the face of the sample. We have in mind specifically here a nucleation event, but it could also be preferential absorption of the laser pulse at defect sites, positions of macromolecules, etc. The boundary conditions chosen are such that the radial outflow of heat from a given hexagon is exactly balanced by the inflow of heat from the neighboring hexagons. Since hexagonal boundary conditions are difficult to deal with we replace each hexagon by an inscribed cylinder and focus our attention on a single cylinder with the boundary condition that the temperature gradient at the outer wall is zero, as shown in Fig.1b. This is not expected to introduce significant errors since the amount of material in the interstices is small and is still treated approximately. We may want to simulate the initial uniform melting of the near-surface region by the laser pulse followed by nucleation and growth events at sites more or less uniformly distributed across the sample, i.e., at the centers of the hexagons or cylinders. To do this, the 2D program is set up so that 1D calculations can be carried out until nucleation of a particular phase has occurred and then 2D calculations are initialized to simulate the growth of the newly formed phase in both the x and r directions. The finite difference grid is taken to be layers of certain thickness in the x direction (typically $\Delta x = 100$ Å and rings in the r -direction ($\Delta r = 100$ --200 Å).

The 2-D heat conduction equation with a source term is straightforward in cylindrical coordinates using enthalpy formulation of heat flow by Rose [12], i.e.,

$$\frac{\partial}{\partial t}(\rho h) = \frac{\partial}{\partial x} \left[K_x \frac{\partial T}{\partial x} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[K_r r \frac{\partial T}{\partial r} \right] + S(x, r, t) \quad (1)$$

With boundary conditions in x direction

$$\left. \frac{\partial T}{\partial x} \right|_{x=0} = 0 ; \quad T_{\infty} = T_{in} \quad (2)$$

Fig.1 Geometry for 2D calculations showing (a) the hexagons with inscribed cylinders and (b) the FD cells in the x and r directions for one cylinder. After a certain number of cells of constant size in the x -direction, additional cells each successively doubled in size are added as needed to satisfy the back boundary condition.

and boundary conditions in r direction

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0, \quad \left. \frac{\partial T}{\partial r} \right|_{r=r_{max}} = 0 \quad (3)$$

$S(x, r, t)$ is the source term, which is given by

$$S(x, r, t) = (1 - R) P(t) \alpha \exp(-\alpha x) \quad (4)$$

where R is the reflectivity of the sample, assumed to be a function of the temperature and phase of the surface, $P(t)$ is the time-dependent intensity of the laser pulse, and α is the absorption coefficient. There is no dependence on r since uniform deposition of laser energy across the radial direction is assumed. Discretization of Eq. (1) was carried out using the classical forward time difference scheme. This scheme gives an explicit method for updating the enthalpies from time step n to $n+1$. Further details of the implementation for discretization of eq.(1) can be found in references [13] and [14].

II. Illustrative applications

(a) Modeling of Nucleation and Propagation of Buried Liquid Layers in a-Si

A test calculation was made using the newly developed 2D LASER8. The sample to be irradiated was composed of an a-Si layer of 415 nm on a c-Si substrate. A KrF excimer laser pulse with full width at half maximum (FWHM) of 40 ns duration and an energy fluence of 0.25 J/cm^2 was used for the source term. At the KrF wavelength (248 nm), the reflectivity of c-Si and a-Si is 0.58 and that of L-Si 0.70. The absorption coefficient was kept constant at $\alpha = 1.8 \times 10^6 \text{ cm}^{-1}$ because of the short wavelength. The temporal and spatial evolution of the various phases is shown in Fig. 2.

As seen in Fig. 2(a), at 27 ns fine-grain silicon (FG-Si) begins to nucleate within the supercooled L-Si in the central surface cell of the cylinder. Before this, a layer of supercooled L-Si was formed on the a-Si layer. The newly solidified material serves as a seed for further growth and the FG-Si phase continues to grow in both x and r directions, as shown in panel (b). However, the growth rates in the x and r directions are not equal. The velocities in the

Fig.2 The nucleation and growth of a Si flake (fine grain Si, FG-Si), formation and propagation of the buried liquid layer (BLL), and calculated flake growth and BLL propagation velocities as a function of time.

r direction are 12.0 m/s and 13.6 m/s, while in the x direction they are 8.0 m/s and 8.6 m/s for $t=38$ ns and $t=46$ ns, respectively, as shown by the numbers in panels (b) and (c). We can understand this phenomenon as follows. Nucleation of FG-Si will release latent heat into surrounding liquid and raise its temperature and the temperature of newly solidified material. Then, a temperature or enthalpy gradient is established due to growth across the interface. Since the thermal conductivity of L-Si is much higher than that of a-Si, heat generated from nucleation and growth of FG-Si is preferentially conducted away in the liquid rather than through the a-Si layer. This is the cause for the anisotropic growth.

The fast growth of FG-Si in the r direction reaches a maximum radius at $t=54$ ns. A small amount of liquid is still left near the surface, and a supercooled liquid layer has been established between the growing FG-Si and the a-Si layer. This buried liquid layer (BLL) is almost flat and propagating at a velocity of 12.5 m/s. The calculated results are consistent with experimental observations [3] in which the BLL was observed to be quite flattened, with no morphological instabilities in the x -direction, to have a thickness of about 10--30 nm, and to be moving at 10 m/s. The BLL continues to propagate at $t=63$ ns and so does the growth of FG-Si. Finally, at $t=72$ ns, the supercooled liquid is exhausted and the whole sample is solidified.

Formation and propagation of the buried liquid layers are related to explosive crystallization [15]. In our case, the FG-Si is grown at the expense of the liquid contained in the buried liquid layer. The latent heat released during this process raises the temperature of the solid phase and the surrounding liquid toward T_c . While crystallization occurs at the back of the buried liquid layer (i.e., the interface between the BLL and FG-Si), previously unmelted a-Si beneath begins to melt since $T > T_a$, resulting in continuous formation of a thin, nearly self-propagating molten layer. The forward motion of the buried liquid layer is driven in part by the difference in the heat of fusion between c-Si and a-Si, $L_c - L_a$, which is positive, and in part by the absorbed laser energy. This means that there is more than enough heat to melt the a-Si beneath. The excess heat will drive the formation and propagation of the buried liquid layer toward the c-Si substrate at an abnormally high velocity, resulting in the explosive crystallization phenomenon. The above simulation results seem consistent with experimental observations [16,17] that explosive crystallization is mediated by a buried liquid layer and from the previous 1D modeling [5]. A more detailed study using the 2D LASER8 on related subjects will be published in a forthcoming paper [14].

(b) Melting Due to Absorption by Localized Defects

The program was modified to calculate the heat flow and phase changes associated with the absorption due to localized, but extended, defects with a high absorption coefficient relative to the matrix in which they are embedded. This was intended to roughly simulate the early stages of the laser ablation of ionic crystals such as MgO. Still using the geometry indicated in Fig.2, the absorption process was changed so that the laser radiation was absorbed only in a region of radius R_a lying within the first few radial FD cells. The amount of energy absorbed is proportional to the area so that it scales as $(R_a/R_m)^2$, where R_m is the maximum radius of the cylinder. Since a nucleation process is not involved, the 2D calculations were initiated at the very beginning of the laser pulse but the radial boundary conditions were kept the same to approximate a more or less uniform distribution of the highly absorbing extended defects. Other parameters were chosen to correspond roughly to those of MgO, however, no attempt at quantitative modeling was made.

Two sets of results are given in Fig.3 for 10 and 40 ns and pulses of 3 and 5 J/cm² as indicated. Because of the low thermal conductivity of MgO, the surface melts very quickly. The diameter of the molten region at 40 ns is $\sim 0.28 \mu\text{m}$ for the 3 J/cm² pulse and $\sim 1.0 \mu\text{m}$ for the 5 J/cm² pulse while the depths are less than half as great. Whether or not MgO ever truly vaporizes seems to be uncertain but apparently it does sublime freely even before it begins to melt. In the laser annealing of GaAs [18,19] it was found that small liquid droplets of Ga formed as gaseous As evolved from the surface of the sample. Similar effects were found in ZnO [19,20] where the evolution of oxygen left the surface covered with a thin layer of Zn after a single pulse from a KrF laser. The coverage was so extensive that good electrical contacts could be soldered on the irradiated spots. In this regard, the results for GaAs and ZnO are so similar to those for MgO that a common mechanism is likely to be involved, namely, the preferential evaporation of the negative ions. However, in ZnO the laser pulse generates a maze of microcracks and this seems to occur in MgO as well, whereas it does not in Si, Ge, and GaAs. Thus, laser ablation of many compounds may not proceed by melting followed by vaporization as is believed to occur in elemental semiconductors and most metals.

Fig.3 Early stages of the laser ablation of materials like MgO. Laser energy is absorbed only in the central cells where the defects are located, as indicated by the arrows in panel (a).

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