Exploring pulsed laser modification and ablation at close-to-atomic scale

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KEYWORDS: ACSM, Molecular dynamics, Pulsed laser, Surface modification

Semiconductor materials play an irreplaceable role in the development of the information technology revolution. The ultra-precision machining of these hard and brittle materials is likely to be achieved by pulsed laser technology rather than traditional machining methods. This paper presents the ablation and modification of GaAs at the close-to-atomic scale in air by pulsed laser. At near threshold energy, the surface modification was detected with a thickness of ~3.5 nm. At high fluences, ablation region was observed in the center. A three-dimensional two-temperature model-based molecular dynamics method was developed to study the laser-material interaction process. The ablation is attributed to the phase explosion mechanism caused by the fast laser energy deposition. In addition, surface modification at the atomic scale was explored by the simulations. This work provides guidance for precision processing of hard and brittle materials towards to atomic and close-to-atomic scale.

NOMENCLATURE

3D = three-dimensional
ACSM = atomic and close-to-atomic scale manufacturing
AFM = atomic force microscope
MD = molecular dynamics
STEM = scanning transmission electron microscope
TTM = two temperature model

1. Introduction

Benefiting from the development of science and technology, the concept of atomic and close-to-atomic scale manufacturing (ACSM) is emerging [1, 2]. This involves a process of material removal, addition, or transfer in the atomic scale. At present, a lot of work is devoted to the nano-cutting of typical semiconductor materials, but the work of surface modification needs to be carried out before cutting, such as laser heating or ion implantation to modify the surface of hard and brittle materials to facilitate processing [3]. Compared with traditional machining methods, pulsed laser processing technology is more suitable for the processing of hard and brittle materials through direct energy deposition [4].

Pulsed laser is a highly efficient micro/nano processing method [5]. Studies show that ablation craters with depth at nano-scale [6] and periodic surface structures at ACS [7] can be generated on semiconductor surface by directed laser irradiation. The removal at atomic layer scale can be made by laser modification at near-threshold fluence and acid-cleaning processing [8]. That show pulsed laser as a powerful tool in ACSM.

The laser-matter interaction is a complex process. The two-temperature model-based molecular dynamics (TTM–MD) method has been used to study the laser-matter interaction process [9]. That is a hybrid atom-continuum model, where TTM presents the continuous temperature field and MD describes the dynamic process in the atomic view. In TTM method, the heat transfer through and between electronic and atomic subsystems are calculated. The dynamic processes from TTM–MD simulations can be used to reveal the mechanisms of melting, solidification, spallation, and phase explosion during laser irradiation process [10].

In this work, the pulsed laser irradiation experiment was carried out on GaAs surface. The ablation and modification at ACS were studied. The TTM–MD method was developed to a three-dimensional (3D) simulation with 3D laser beam energy deposition. The mechanisms respond for ablation and modification were investigated by the developed 3D TTM–MD method. Finally, the minimum modification depth at ACS was explored.

2. Experiment and Theoretical Analysis on the Pulsed Laser Irradiation

2.1 Experiment

The ultraviolet laser with wavelength of 355 nm and pulse duration of 20 ns was used. The detailed description was reported in previous article [8]. The sample is a n-type GaAs wafer. The irradiated surface is the (001) face.

With the pulse energy of 3.3 μJ, the irradiated sample morphology measured by atomic force microscope (AFM) is shown in Fig. 1(a). There is an ablation crater in the center, where microcolumn structures are distributed. Modification zone is detected around the crater, which shows local melting and solidification. The size of ripples decreases along the radial direction due to the Gaussian laser beam profile. At the energy of 2.9 μJ, the laser-affected zone shown in Fig 1(b) is higher than the initial surface. The result indicates the laser induced modification on GaAs surface rather than direct material removal. The non-melting modification appearing at the edge of the laser-affected zone is expected to be attributed to surface amorphization and oxidation. Fig 1(c) presents the AFM cross-section profiles at the two cases, which describes the different of ablation and modification at the height profiles.

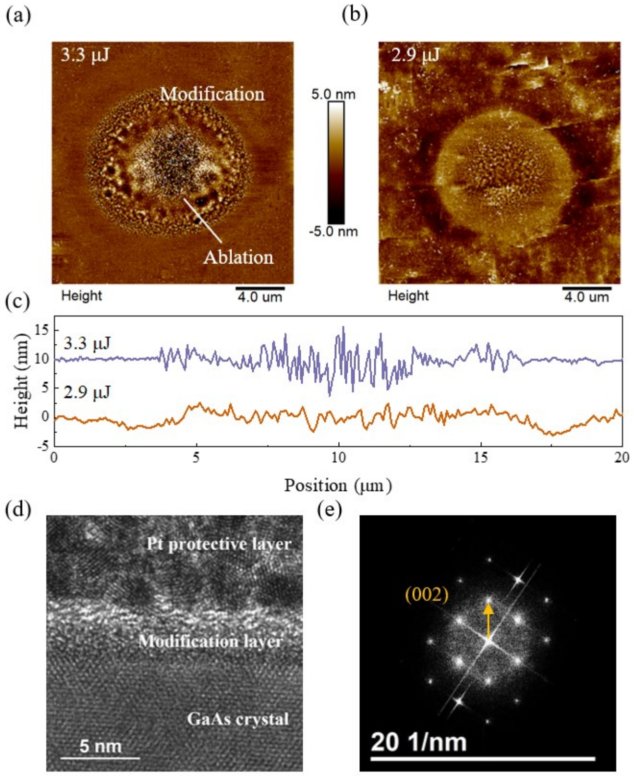

Fig. 1 Experiment results of 355 nm laser pulse irradiation on GaAs. Surface morphologies at the laser energy of (a) 3.3 μJ and (b) 2.9 μJ. (c) AFM cross-sections profiles. (d) STEM measurements sampled at the irradiated surface with 2.9 μJ laser pulse. (e) Selective-area electron diffraction pattern in the region of GaAs crystal

The subsurface damage at the laser-affected zone with 2.9 μJ laser pulse was measured by scanning transmission electron microscope (STEM). The high-resolution transmission electron microscopy image is presented in Fig. 1(d). The result shows Pt protective layer, laser modification layer, and GaAs crystal. The detected average thickness of the modification layer is 3.5 nm. The selective-area electron diffraction pattern shown in Fig. 1(e) shows the crystal structure and the crystal orientation.

2.2 Three-Dimensional Model to the Laser Irradiation

Generally, the 1D laser energy is uniformly deposited on the irradiated target surface, ignoring the transverse propagation of stress and temperature. The details of the TTM-based MD method have been reported elsewhere [11]. Here, the 3D TTM–MD method is developed to realize laser irradiation by depositing 3D Gaussian beam profile on the coarse-grained electronic temperature grid. Fig. 2(a) shows the simulation setup. The simulation box contains 4,536,000 atoms. The (001) Ga face was set as a free surface perpendicular to the x-direction. Periodic boundary conditions were applied along the y- and z-directions.

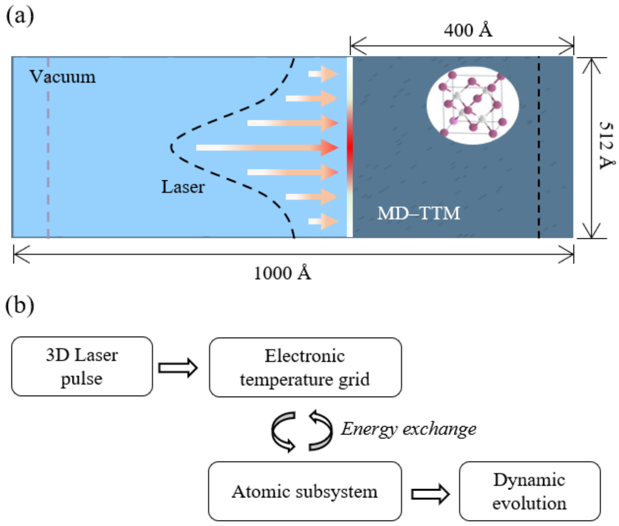

Fig. 2 The schematic diagram of the 3D TTM–MD simulation system. (a) Model settings, (b) flow chart

Fig. 2(b) shows the energy transfer in the 3D TTM–MD system. The pulse energy is absorbed by the electronic subsystem by the coarse-grained electronic temperature grid. The electronic temperature grids are evenly divided along the three directions with dimensions of 100×37×37. There are ~83 atoms in each grid, which is enough to calculate the statistical temperature of the corresponding atomic subsystem. Then, the energy is exchanged between the electronic and atomic subsystems according the two-temperature model. Finally, the dynamic evolution is calculated in the MD part based on the Tersoff potential. The timestep is 1 fs.

2.3 Simulation Results

Fig. 3 shows the simulated atom snapshots illustrating the laser irradiation on GaAs at the fluence of 10 mJ/cm^2. A local atomic sliced layer with a thickness of 2 nm was used to display the dynamic process of the laser-GaAs interaction. At 5 ps, the material closed to the surface undergoes a phase transition from crystalline to amorphous. At 10 ps, a few atoms were desorbed from the surface. At 20 ps, the surface material is decomposed into nanoparticles, producing an ejection of ablation plumes. It can be seen from the aerial view in Fig. 3 that the target surface in the first 20 ps can be divided into an ablation removal zone and a heat-affected zone, which is consistent with the experimental results.

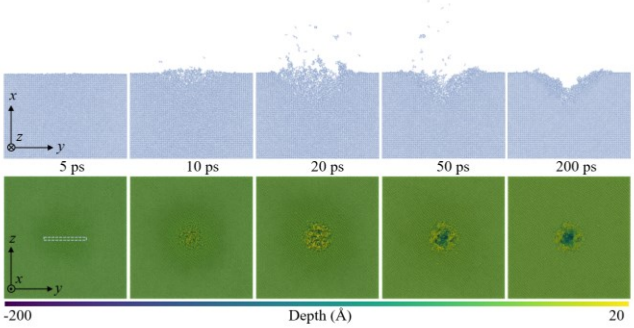

Fig. 3. Snapshots of the structure evolution at the fluence of 10 mJ/cm^2. Upper: the side views for a 2 nm thick sliced layer sampled from the rectangular box marked with dash line, and the simulated atomic configuration is colored by atoms, bottom: the aerial view snapshots of atomic configuration colored by the position along the *x*-direction.

According the simulated dynamic process, the ablation removal of GaAs is expected to be attributed to the phase explosion mechanism. To prove the mechanism, a constant pressure MD simulation was conducted with a crystal box containing 4096 atoms. The simulation system was heated until the explosive boiling occurs. Fig. 4(a) shows the volume-temperature curve, that gives a critical temperature of 2850 K. Generally, the 90% of the critical temperature is determined to be the threshold for homogenous boiling of a system [12]. The size distribution of the clusters and local structure after explosive boiling is shown in Fig. 4(b). The size distribution is consistent with that of ablation plumes as shown in Fig. 4(c) and Fig. 4(d). The size distribution of the clusters with low atomic number can be described by the power law $Y(N) \propto N^{-\tau}$.

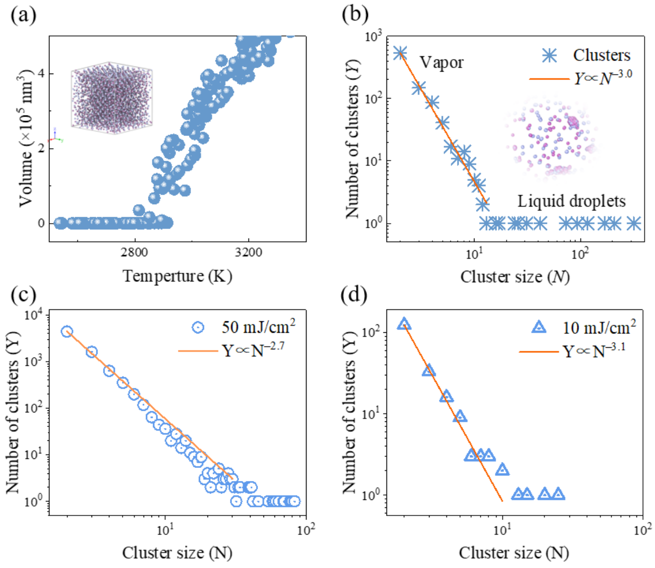

Fig. 4 The MD simulations for phase explosion. (a) the volume-temperature curve with the inset figure of a metastable liquid system, and (b) the size distribution of clusters after the phase explosion with the inset figure describing the two-phase mixture of liquid and vapor. Size distributions of laser ablation plumes at (c) 50 mJ/cm^2 and (d) 10 mJ/cm^2

Fig. 5 shows the different in the cross-sectional structure at the three laser fluences. The snapshots for a sliced layer at the laser fluence of 50 mJ/cm^2 shows that the material was decomposed into Ga-rich layer and As at the bottom of the ablation crater. The precipitation of As is an important process during laser ablation as described by micro-Raman spectra in previous report [13]. At 8 mJ/cm^2, the modification is different with ablation. A thin layer with a thickness of ~2 nm on the surface is modified by laser energy deposition, accompanied by a small number of atoms desorption from the surface. That is consistent with the experiment. Note that, the oxidation plays a role in the laser modification in the experiment. At near-threshold, the modification was observed at the scale of ~2 atomic layers, proving the potential of pulse laser in atomic and close-to-atomic scale manufacturing.

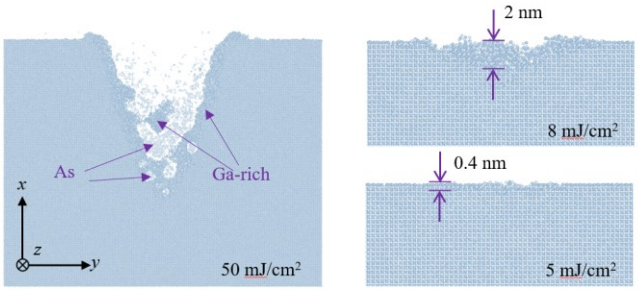

Fig. 5 Local slices of the simulated laser-affected zone at the energy of 50, 8, and 5 mJ/cm^2

3. Conclusions

The ablation and modification at close-to-atomic scale were studied by pulsed laser irradiation. A 3D TTM–MD method was developed to study the mechanisms respond for laser ablation and modification at ACS. The mechanism of ablation at high fluences is phase explosion, in which materials are explosively decomposed into a two-phase mixture of liquid and vapor. The modification is attributed to laser-induced amorphization, and thermal oxidation in air may play a role. The work provides a guidance for laser-matter interaction, as well as the laser processing in ACSM.

ACKNOWLEDGEMENT

This study was supported financially by the National Natural Science Foundation (Grant No. 52035009 and 52105475)

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