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Analysis of gallium phosphide nanoindentation by means of molecular dynamics simulations

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Abstract

For the development of new designs of micro-optical devices, semi-conductor materials offer enhanced optical properties favouring applications in the domain of solid immersion lenses, resonators, and LEDs. However, the hard-brittle material properties critically influence single-point diamond machining processes. For example, in order to cut in ductile regime, a high-pressure phase transformation (HPPT) to a ductile phase is required, otherwise brittle behaviour compromises the surface integrity of the material. That is the case of gallium phosphide (GaP). For a fundamental understanding of HPPT of GaP, this paper aims at validating an existing Molecular Dynamics (MD) force field (FF) for GaP under shear stress loads. To this aim, MD simulations alongside nanoindentation experiments are proposed to validate the FF. MD simulations were performed using this FF for the GaP substrate and a spherical FF to emulate an indenter tip with 3.5 nm radius and velocity of 0.4 Å/ps (40 m/s). Nanoindentations were conducted with a Berkovich indenter until a maximum load of 10 mN with load rates of 0.1 mN/s, 0.5 mN/s and 1.0 mN/s. Furthermore, Atomic Force Microscopy (AFM) measurements of the generated indents were conducted alongside the analysis of load-displacement curves. With the MD simulation results, it was possible to estimate the material hardness, predict the formation of pile-ups and pop-in events induced by the presence of dislocations and phase transformations. The experimental results are in accordance with simulation results. Furthermore, the experimental results indicate the occurrence of HPPT from zincblende to Sc16. The results using the proposed FF proved to be in accordance with the events of nanoindentation experiments and literature. Therefore, the FF can be further employed e. g. in cutting simulations.

Gallium Phosphide, Nanoindentation, Molecular Dynamics Simulations, Vashishta potential, Semiconductor.

1. Introduction

New designs for micro-optical devices can emerge with the aid of semiconductors materials with enhanced optical properties. Among these semiconductors, GaP has a high refractive index from middle infrared to the beginning of the visible spectrum (3.3 for a 600 nm wavelength), direct band gap (meaning it can emit light when under an electric potential difference), piezoelectric behaviour, and mechanical properties comparable to GaAs [1]. Currently GaP is mainly applied as a green LED, as well as red or orange LED when combined with other materials, but new applications have emerged. A new application is a prototype resonator that converts microwave radiation in the visible spectrum, which is applicable to quantum computer grids [2]. Another new application is solid immersion lenses (SIL) with small apertures (< 1 mm) [3]. For SIL and other optical elements with complex shapes and optical quality surfaces, machining with a single crystal diamond tool is required. However, as shown by Lohrke et al. [3], a high tool wear was present during UP-turning, therefore limiting the amount of GaP lenses produced by a single tool. In order to understand the wear mechanisms, it is necessary to investigate the behaviour of GaP under plastic deformation and its phase transformations. This can be achieved by using MD, which is a widely used method to study material behaviour in the atomic scale. MD simulations of the nanoindentation process can be used to investigate the plastic behaviour of materials during deformation caused by the indenter.

Nanoindentation is a method to analyse materials and to generate data about material properties. During the nanoindentation process, the main load is a hydrostatic pressure [4], but shear stress is significantly present. Hydrostatic pressure induces a HPPT from a brittle phase into a ductile phase. This is necessary to achieve an optical surface quality when machining brittle semiconductors by means of UP-machining operations using diamond tools. However, shear stress is more significant than hydrostatic pressure for these operations.

In a classical approach, the MD method considers the atoms of a system as rigid spheres, whose dynamics are simulated by the numerical integration of the classical equations of motion. System's energy is described by the kinetic and potential components. The latter is defined by a set of equations and specific parameters for each atom type present in the system, the so-called force field (FF). Through the in integration of these FFs for every atom using short time intervals MD simulations can describe the trajectories of atoms. MD simulations can also simulate unknown phase transformations, which is an advantage over other approaches, such as finite element methods. However, this depends on the accuracy of the FF on reproducing the crystallographic structure of the material by its equations dealing with the bonded terms (bond stretching, angle bending and torsional barriers).

A FF for GaP was developed by Ribeiro et al. [6] using the Vashishita et al. [7] potential energy function (PE), which is

suitable for ceramics and semiconductors materials. Simulations with this FF was able to describe some of GaP phase transformations under pure hydrostatic loads [6, 8], but the shear stress was not considered. Therefore, the main objective of this work is to analyse GaP behaviour during the nanoindentation by using this FF in a MD simulation and compare the generated data with nanoindentation experimental results.

2. Simulation Methodology

The simulations were conducted using the FF for GaP presented by RIBEIRO-SILVA ET AL. [6]. The GaP substrate was divided in three layers: fixed atoms; canonical ensemble or NVT atoms; and microcanonical ensemble or NVE atoms, as presented in the **Figure 1**. The layer with NVT atoms emulates the body capacity of absorb heat, since the temperature T is kept constant at 300 K. NVE atoms form the layer of interest, where the energy E is kept constant. The number of atoms N and the volume V is kept constant for both ensembles. A LAMMPS function was used to create a spherical force field to emulate an indenter.

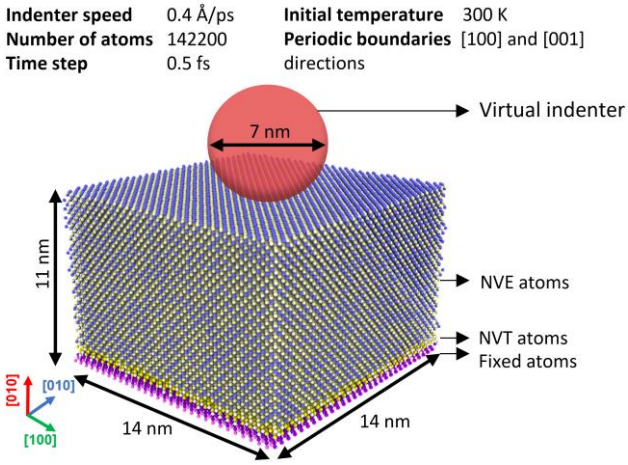

Figure 1 Nanoindentation simulation model

2.1 Stress Evaluation

The applied method to calculate the hydrostatic stress consists of converting an atomic measurement of stress, the virial stress S_{ab} to the Cauchy stress tensor and then use the von Mises criteria [4]. The virial stress was calculated through LAMMPS® software algorithm as a product of the atomic volume V_i and the atomic stress σ_{ab}. Hence the output value S_{ab} was divided by the atomic volume. In this sense, the virial stress six components of the atom i can be obtained by Equation 1:

$$\sigma_{abi} = \frac{S_{abi}}{V_i} \qquad 1$$

where a and b take the values of x, y, and z in order to generate each one of the six components and V_i is the atomic volume of the atom i.

Spatial and time averages were performed. Time average was performed along 2.5 ps for each atom, and spatial average within a 5.45 Å radius sphere around each atom.

2.2 Structure Identification

Three different algorithms were used in combination to identify atomic structures, all of them are present in Ovito® software: dislocation extraction algorithm (DXA), polyhedron template matching (PTM), identify diamond structure (IDS), which also calculates the radial distribution function (RDF) and the coordination number (CN) [9,10].

3. Experimental Methodology

A total number of 150 nanoindentations were performed in a 300 µm thick GaP sample using a Hysitron TI 950 nanoindenter by BRUCKER INC., USA, with a Berkovich indenter. Beforehand the sample was cleaned with First Contact by PHOTONIC CLEANING TECHNOLOGIES, USA. They were divided in 3 groups of 50 indents each. Three different load rates P_r = 0.1 mN/s, 0.5 mN/s, and 1.0 mN/s were used. The indentations were spaced 15 µm apart from each other and the groups were separated by 40 µm. The indentations were performed in force-controlled modus with a load P = 10 mN. The investigation of JIAPNG ET AL. [11] was used as reference to establish the lowest load rate value of P = 0.1 mN/s. This load rate used by the authors while indenting silicon were sufficient to generate cracks and allowed a comparison with MD simulation. Since simulations were performed using indentation speeds higher than experimental ones, higher load rates of P_r = 0.5 mN/s and P_r = 1.0 mN/s were also tested.

For every group, two indentations were measured with the atomic force microscope (AFM) NaniteAFM by NANOSURF, Switzerland. The main goal of the AFM measurements was the observation of pile-ups or sink-ins.

4. Simulation Results

In **Figure 2**, a hydrostatic pressure above 15 GPa in a small region underneath the indenter can be observed. The phase transformation using the FF is expected to happen just above this value at 300 K for pure hydrostatic pressure loads. Therefore, as shown by GOEL ET AL. [12] for SiC nano-cutting MD simulations the hydrostatic pressure that is required to induce an HPPT is reduced in the presence of shear stress.

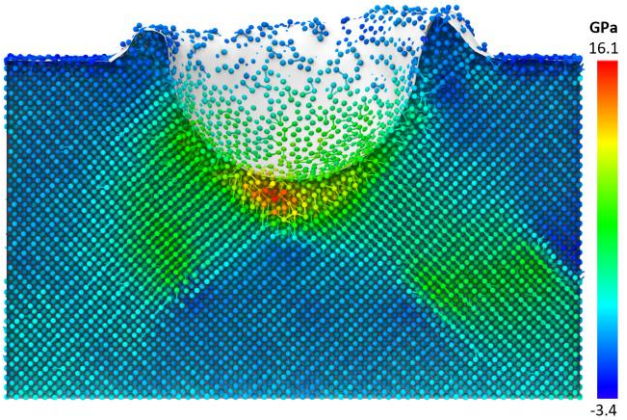

Figure 2 Hydrostatic pressure at maximum load

As it is shown in **Figure 3** (a), the coordination analysis provided by the IDS algorithm shows CN 6 atoms just under the indenter surrounded by CN 5 atoms. β-tin structure has CN 6 while zincblende CN4. CN 5 appears on the interface of them. This finding is analogous results of MD nanoindentation simulations of silicon conducted by JIAPENG ET AL. [11]. In **Figure** 3 (b) simple cubic structures are found in the region under the indenter with the PTM algorithm. This happens, because the expected β-tin structure is not available for this algorithm, but it was possible to identify how this structure is perceived by the algorithm by applying it to a system with only β-tin structure at 0 K. In this case, most of the atoms were perceived as belonging to a simple cubic structure with some belonging to a zincblende structure. Therefore, the post process algorithms indicated once

more the presence of a β-tin phase in GaP during the simulation. By removing the phosphorous atoms in **Figure 3** (c) the zincblende structure is reduced to a face centred cubic (FCC) structure and the β-tin structure to a deformed body centred cubic (BCC) structure, which was perceived by the PTM as a BCC structure. Hexagonal compact (HC) structures were also detected. They seem to match the region with CN 5 atoms.

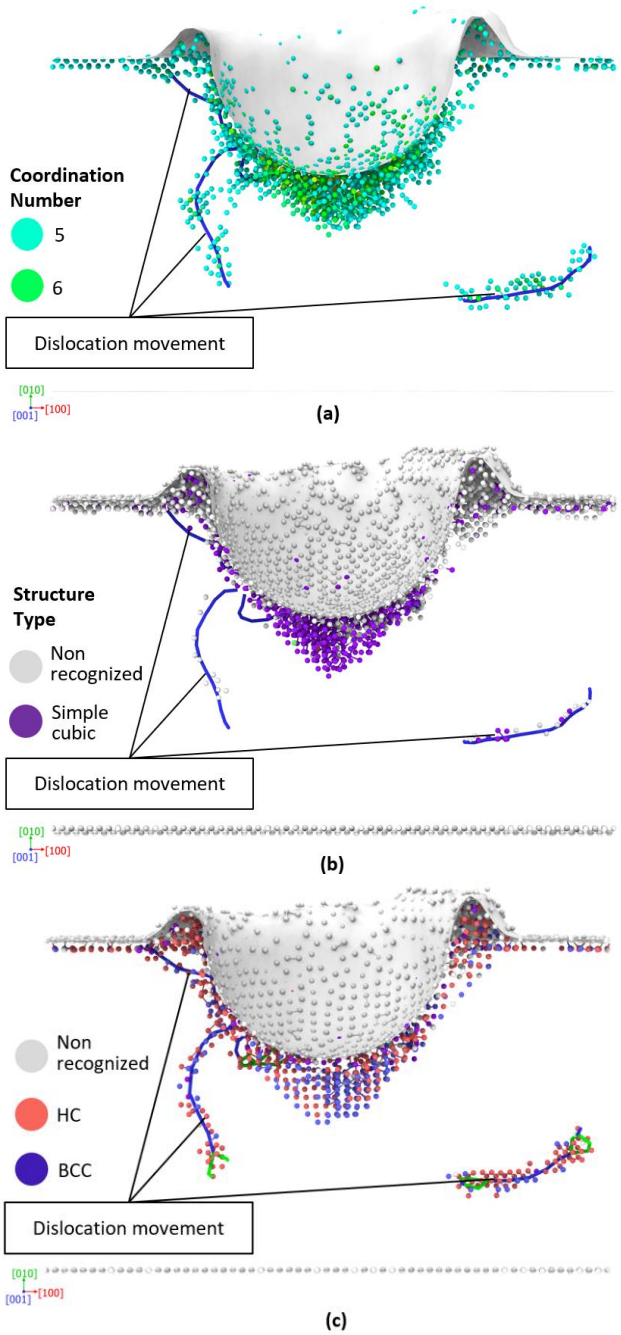

Figure 3 Structure identification sequence at maximum load: (a) coordination analysis showing only CN 5 and 6, (b) PTM removing zincblende structure, and (c) PTM after the removal of the phosphorus atoms and FCC structure

When a discontinuity on loading curve appears as a line parallel to displacement axis, a phase change, a discontinuity or both events are present. To this discontinuity is given the name pop-in. When similar event occurs on unload curve, the discontinuity is called pop-out. In contrary of pop-ins, pop-outs are always an indication of phase transformations. The P-h curve (load X displacement curve) of the simulation in **Figure 4**, shows the occurrence of several pop-ins. No clear pop-out was observed. The first pop-ins are shorter and happen before the presence of the first dislocation. The second type happens when dislocations are present (plastic regime). In the latter, the formation of a new phase under the indenter tip is compromised by the presence of dislocations. When the region under the indenter is free of dislocations, the phase transformation takes place once more.

The hardness value calculated at the end of the loading curve was 10.5 GPa (**Figure 4**) with a maximum of 10.8 GPa close to the end. The calculated hardness values are close to the values H = 10.9 ± 0.2 GPa of GRILLO ET AL. [13] at 10 mN maximum load. These same authors observed a hardness H = 12.5 ± 0.2 GPa for P = 1 mN and CHIU ET AL. [14] observed H = 12.5 ± 1.2 GPa for P = 6 mN. A possible explanation for a hardness value lower than experimental one's is the temperature increase along the simulation. Without an indenter to absorb the temperature on the simulation, the hardness may decrease due material softening.

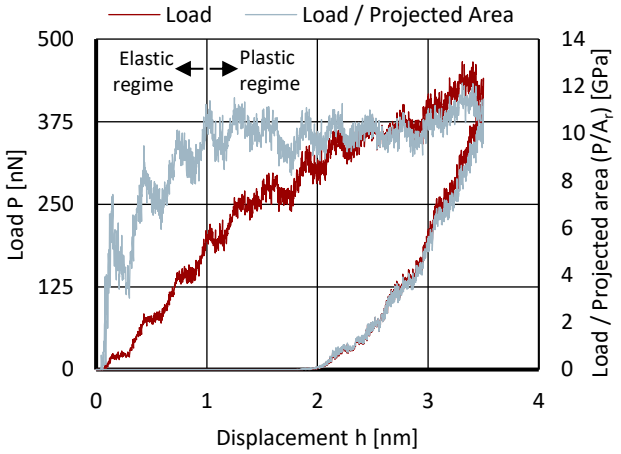

Figure 4 (a) P-h curve and (b) (P/A_r)-h curve of a nanoindentation simulation of GaP

5. Experimental Results

Experimental P-h curves for different load rates are shown in the **Figure 5**. Long pop-ins close to P = 2 mN can be seen in every nanoindentation. After that, a series of shorter pop-ins can be observed.

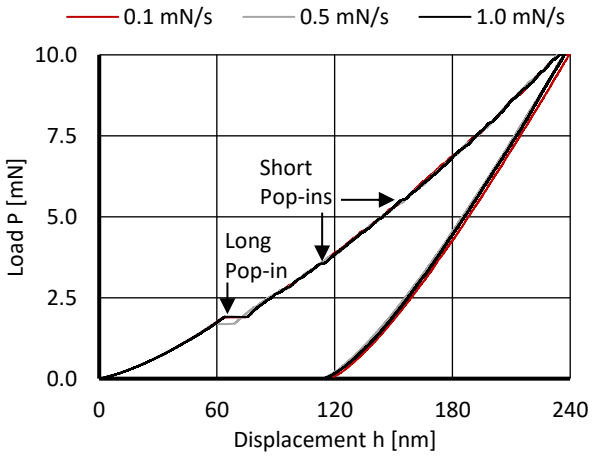

Figure 5 P-h curve from an experimental nanoindentationn of a 10 mN maximum load at different load rates: 0.1 mN/s, 0.5 mN/s, and 1.0 mN/s

When the load is divided by a theorical projected area of the Berkovich indenter, longer pop-ins appears on average between

14 GPa and 19 GPa. Since experimental data show the phase transition from zincblende to Sc16 at 14 GPa, this long pop in can indicate this phase transition. *Ab initio* simulations reinforce that by suggesting this transformation between 15 GPa and 23 GPa under pure hydrostatic pressure load. The FF used for the MD simulations cannot predict this is a phase transformation. Instead, it predicts a direct transformation from the zincblende to a β-tin phase at 15 GPa at 300 K [5]. Although the zincblende-Sc16 phase transformation is not present during simulations, the hardness calculated is close to experimental hardness. The projected area used to calculate the pressure values on pop-ins does not consider the displacement correction proposed by Oliver and Pharr [15], since the slope can only be calculated at the very end of the loading stage. A cyclic nanoindentation would be necessary to confirm the pressures for this pop-in.

The short pop-ins are possibly a formation due to the presence of dislocations. This behaviour can also be seen in the simulation, where the dislocations under the indenter tip limits the phase transformations.

The AFM measurements have shown material pile up (**Figure 6**) on the indentations. This corroborates with the simulation and demonstrates the plastic deformation of the material. The hardness values found (11.0 ± 0.2 GPa for 1.0 mN/s, 11.1 ± 0.2 GPa for 0.5 mN/s, and 11.2 ± 0.6 GPa for 0.1 mN/s) were similar to the one found by Grillo *et al.* [13].

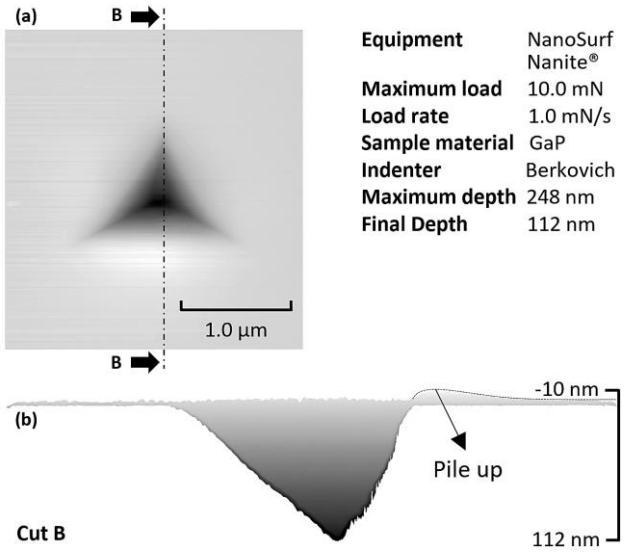

Figure 6 (a) Post-processed image with amplitude and phase data from a 10 mN, 0.1 mN/s nanoindentation, and (b) Cross section view

6. Conclusions

MD simulations of the nanoindentation process alongside nanoindentation experiments in GaP were performed. The simulation results have shown a hardness value close to the values found experimentally and in the literature. Two different pop-ins groups were also observed in the simulations. The first group happened during the elastic phase, where phase transformations were present. The second group happened during the plastic phase where dislocations were present under the indenter tip. During nanoindentation experiments, a major pop-in was observed in every indentation and possibly correspond to the zincblende to Sc16 phase transformation. Pile-ups were observed in AFM measurements, which are an evidence of the plastic deformation of GaP.

7. Outlook

For future works, additional MD simulations of the nanoindentation of GaP with different indenter radius would confirm the simulation capacity of estimate material hardness. The results presented is this work also indicate that the used FF is suitable for simulating the cutting process of GaP with a diamond tool.

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