

Original Research Paper

Understanding Material Deformation in Nanoimprint of Gold using Molecular Dynamics Simulations

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Abstract: Material deformation in nanoimprinting is explored through Molecular Dynamics (MD) simulations. Understanding the behavior of substrate material during the nanoimprinting process is imperative for high resolution nanoscale pattern transfer. Nanoimprinting of the gold has the potential to make significant impact in diverse areas such as microelectronics and biomedical research. The deformation of gold during nanoimprinting is studied for varying depths of mold from the density profile mechanics viewpoint. The effects of varying imprint depth at a constant imprint velocity and temperature on the deformation behavior are investigated. It is observed that for higher imprint depth the spring back effect is substantial. Localized variations to density of the gold substrate were observed during the mold loading phases. Higher imprint depths displayed an increase of density up to 1.55 times the normal density of gold. This research provides insight into the deformation mechanism of gold substrate based on density profile variations and spring back effect.

Keywords: Density Profile, Imprint Depth, Molecular Dynamics, Nanoimprinting, Spring Back Effect

Introduction

The manufacturing of nanoscale structures is vital for the development of various types of functional nanodevices. Nanoimprint lithography (NIL) is a nanofabrication technique that facilitates fabrication of nanopatterns to produce integrated circuits, miniaturized devices, drug delivery nanoneedles (Chou *et al.*, 1996; Chou and Krauss, 1997). Nanoimprint lithography is a versatile technology because of its high resolution, low cost and high throughput. In NIL, the precisely patterned mold is pressed into the substrate to replicate the mold topography. Nanoimprint lithography was originally developed for imprinting on polymers. However, direct nanoimprinting on metals is of great interest due to its potential applications (Pease and Chou, 2008). The micro/nanodevices made from metal hold advantages in applications such as gratings for optical components, polarizers, electromagnetic relays and optical isolators (Vigneswaran *et al.*, 2014; Yang *et al.*, 2014). Due to its superior electrical and thermal conductivity properties gold is an attractive candidate for the nanopatterning based on its widespread use in the electronic industry. Recently, gold has been used in the nanofabrication of medical sensors that detect biomolecules and diagnose specific diseases (Wong *et al.*, 2013).

Nanoimprint lithography has been applied to fabricate devices for optical, photonics and many other applications in Micro Electro Mechanical Systems (MEMS) (Wu and Hou, 2018). Prior studies have provided insights on the effect of temperature on the imprint force for polymers (Kang *et al.*, 2010). The atomic scale mechanism prompting the nanoimprint process for gold is unexplored. This includes investigating the density variation during material deformation and effect of imprint depth on the imprint quality. Specifically, the density variation during the plastic deformation of a metal during imprinting plays a vital role in determining the performance of the fabricated nanopatterns. Therefore, a fundamental understanding of the nanoimprint mechanism for gold is vital for fabricating high quality nanopatterns. Some researchers have explored direct nanoimprinting of gold with nanoindentation equipment. However, this work mainly focused on the experimental analysis (Zhang *et al.*, 2014). Kwon and Kim (2016) presented the correlation between the temperature and the imprint force. They revealed that when temperature was increased the imprint force required was reduced. Although, experimental approaches explain outcomes of different imprint conditions, computational models provide a fundamental understanding of the process mechanics. Finite Element Method (FEM) has been

applied to understand the phenomenon of nanoimprinting (Yasuda *et al.*, 2010). However, the FEM is limited to the macro scale phenomenon and the continuum approach does not yield conclusive insights at the nanoscale regime (Cordeiro and Desai, 2016). Molecular dynamics modeling is an atomistic simulation to analyze the nanoscale phenomena (Cordeiro and Desai, 2015; 2016; 2017). Many researchers have focused their efforts on finding the optimal process parameters (Hsu *et al.* 2005), mold and pattern breakage mechanism (Yasuda *et al.*, 2010) and effects of nanoscale defects on mold fracture (Lin and Yu, 2017). A group of researchers have employed MD simulations to study the effects of system temperature, indentation force and surface orientation in the nanoindentation process to analyze the mechanical properties of the materials (Hsiung *et al.*, 2009; Jiao *et al.*, 2018). Quang-Cherng *et al.* (2004) investigated the effect of mold geometry on imprint forces and internal energies for nanoimprinting of copper. Based on load-distance and energy-time plots they concluded that the deformation force and the internal energy is high for greater taper angles. Also, the largest stress distribution was observed near the contact of mold and substrate.

This research investigates the material deformation behavior of gold substrate with a silicon mold. The effect of varying the imprint depth on the density variation in the gold substrate was studied. Understanding the density distribution within a nanoimprinted substrate is vital to the output quality of the reproduced pattern. This paper provides the fundamental understanding of the nanoimprint process with respect to metallic substrates wherein the spring back effect plays a dominant role in the final pattern transfer process.

Methodology

This section presents the simulation conditions, force fields and simulation analysis methods used. All the simulations were executed within Nanoscale Molecular Dynamics (NAMD) source code (Phillips *et al.*, 2005). Visual Molecular Dynamics (VMD) was used for model development, visualization (Humphrey *et al.*, 1996). Both NAMD and VMD were developed by the Theoretical and Computational Biophysics Group in Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign. The simulations were run on a 64-bit Linux Fedora 27 system with Graphical Processing Unit (GPU) board (2 NVIDIA K40) with 2880 cores. The density profile tool plugin in VMD was used for analyzing the results of the simulations (Giorgino, 2014).

Figure 1 depicts the nanoimprint process for gold substrate and silicon mold. The nanoimprint process was divided into six steps which include system temperature ramp up, stamp loading into the substrate, stamp hold, system temperature ramp down, relaxation of the system

and stamp unloading. Studying the dynamic behavior of substrate during these steps is important for successful pattern transfer.

In this study, the Lennard-Jones potential was used to simulate the atomic force interactions between mold and substrate which is defined by Equation (1):

$$E_{Lj} = 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

where, E_{Lj} signifies the pair potential energy function. The ϵ_{ij} and σ_{ij} are well depth and finite distance at which the interparticle potential is zero between a non-bonded pair of atoms i and j respectively. r_{ij} corresponds to the distance between atoms i and j . The material properties and Lennard-Jones potential function parameters for this research are given in the Table 1.

All simulations were performed with a 1 fs integration time step. Data were recorded every 0.005 ns. The cutoff distance for Van der Waals interactions was 12 Å.

Molecular Dynamics Model

Figure 2 shows the MD model and the process steps for the nanoimprinting of gold. The gold substrate had 64512 atoms with dimensions of 10 nm x 10 nm x 5 nm. The Si mold had 22048 atoms with a tooth depth of 5 nm and tooth width of 3.8 nm. Periodic boundary conditions were applied in both x and y directions. Two layers of atoms at the bottom of the gold substrate were fixed. Figure 2a depicts the first step of the process in which the temperature of systems was raised to 473 K, which is the recrystallization temperature of the gold. During initial position and temperature ramp-up phase the atoms of gold were in the same position. Figure 2b shows the actual process of imprinting, where the mold was loaded into the substrate at a constant velocity. Steered molecular dynamics was used to impart a velocity of 50 m/s to the mold. The mold was held in the substrate for 0.5 ns to initiate pattern transfer. In this phase, the gold atoms clustered around the mold tooth due to imprinting force. However, the atoms in the rest of the substrate geometry maintain their original position. In this position, the temperature of the system was gradually ramped down to 293 K for 0.5 ns. On reaching room temperature (293K) the system underwent relaxation for 0.5 ns.

Table 1: Material properties and LJ parameters

Parameter	Substrate (gold)	Mold (silicon)
ϵ , kcal/mol	-0.0390	-0.310
σ_{ij} , Å	3.6900	4.270
Melting point, K	1337.0000	1687.000
Density, kg/m ³	19300.0000	2328.000
Lattice constant, Å	4.0788	5.431

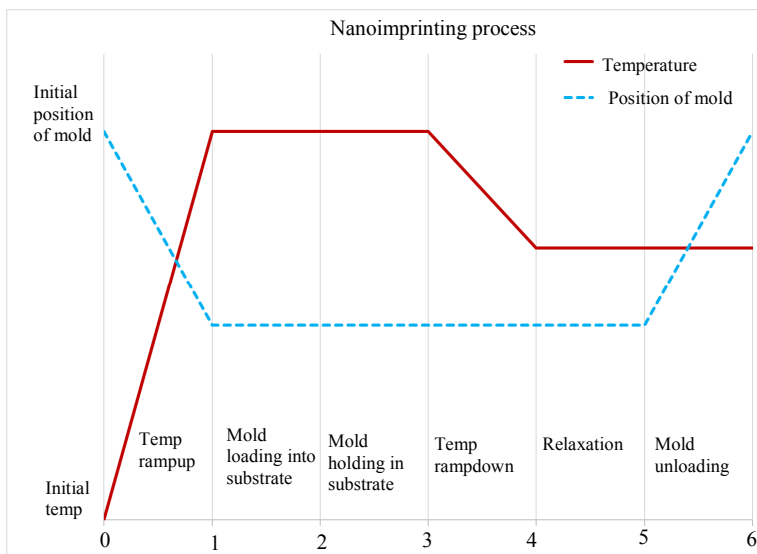


Fig. 1: Phases in the nanoimprint process

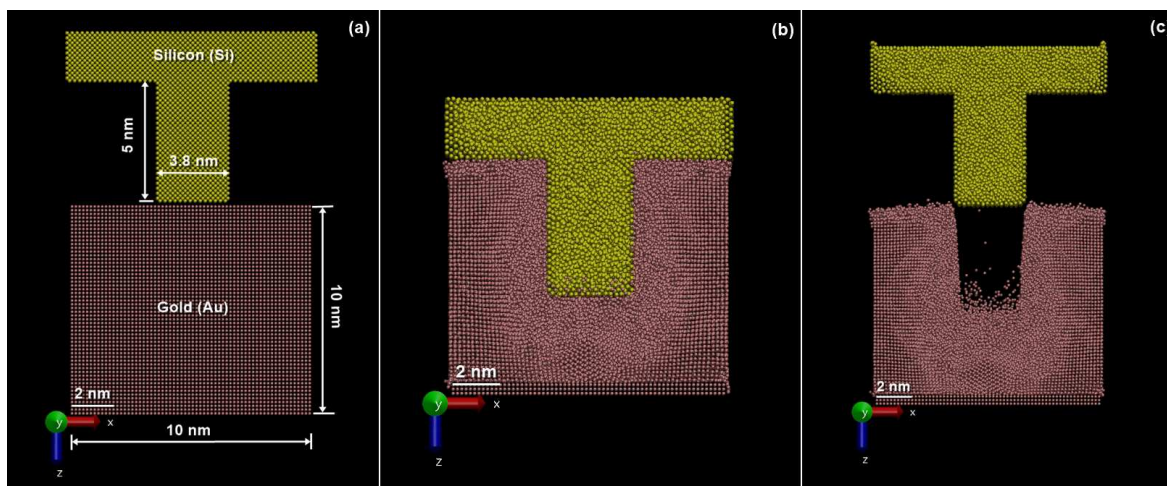


Fig. 2: Phases in nanoimprinting process (a) Initial position and temperature ramp up (b) Mold loading into substrate, mold hold, temperature ramp down and relaxation (c) Mold unloading from the substrate

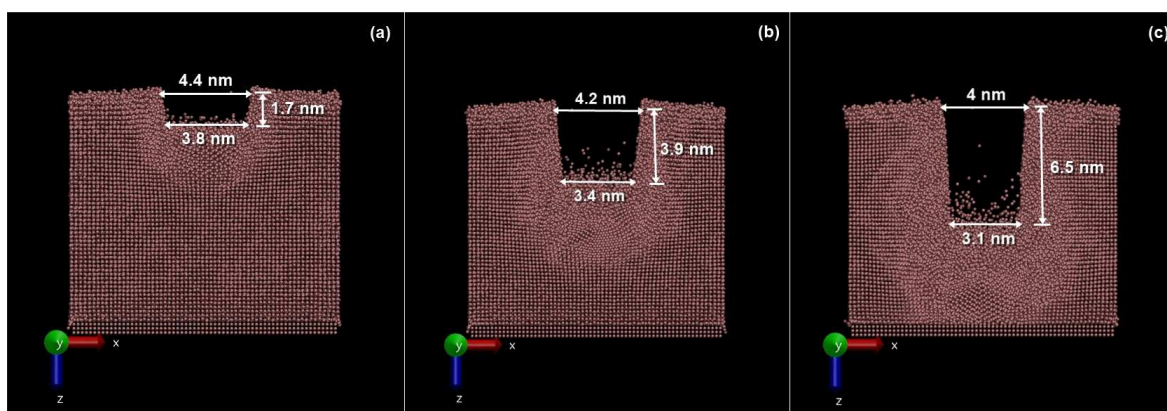


Fig. 3: Substrate after nanoimprinting process (a) 500,000 time steps (b) 1 million time steps (c) 1.5 million time steps

The plastic deformation and relaxation of the gold substrate occurred during the phases of mold loading, mold holding and temperature ramp down phase in the process. After this phase the mold was unloaded from the gold substrate at a velocity of 50 m/s. Figure 2c shows the final deformation of the gold substrate after the nanoimprint process. The gold substrate underwent recrystallization to retain the shape of the mold tooth. A spring back effect was detected on the imprinted pattern when the mold was unloaded from the substrate.

Results and Discussion

Effect of Imprint Depth on Deformation Geometry and Spring Back Effect

The silicon mold was imprinted into the gold substrate at different imprint depths namely; 500,000 time steps, 1 million time steps and 1.5 million time steps. Figure 3 depicts the shape of the imprinted substrate at different depths. It was revealed that as the number of steps increase (i.e. as the mold imprints deeper into the substrate) the resultant negative replica shape of mold in the substrate gets narrower. The original width of the mold tooth was 3.8 nm. For a perfect replication of the mold, an imprinted substrate would form a cavity of 3.8 nm in width. However, due to material spring back phenomenon in metals the imprinted dimension would be lower than 3.8 nm as evident from Fig. 3. The width of the 500,000 steps imprint at the bottom and top of the imprinted cavity were 3.8 nm and 4.4 nm, respectively. Whereas the cavity for 1 million steps measured 3.4 nm and 4.2 nm, respectively. Finally, the imprint cavity for 1.5 million steps measured 3.1 nm and 4 nm, respectively.

Figure 4 describes the variation in the imprinted cavity for each simulation condition. At the end of mold loading phase, the imprint depths for 500,000 time step, 1 million time step and 1.5 million time step were 1.7 nm, 3.9 nm and 6.5 nm respectively. The final imprinted depths after unloading the mold for 500,000, 1 million and 1.5 million time steps were 1 nm, 3 nm and 6 nm respectively. It is important to note that for 1.5 million time step simulation the mold tooth was imprinted beyond its depth (i.e. 5 nm) into the substrate. This resulted in an imprinted depth larger (6 nm) than the original depth (5 nm) of the mold tooth. Thus, based on both shrinkage in the dimensions along the lateral and depth directions for the imprinted substrate a spring back effect was confirmed. Also, some substrate atoms were dislodged from their imprinted positions due to adhesion energies between the mold and substrate atoms. This was prominently observed in the region of higher

densities as compared to the rest of the mold geometry. This was due to the compressive forces subjected by the mold which increased the localized density of atoms in the substrate. Further, the substrate was stabilized by holding the mold in the loaded position at the recrystallization temperature and gradually ramping down the temperature to the room temperature.

Effect of Imprint Depth on Density Profile of Gold Substrate

The density profile of the substrate for different imprint conditions was evaluated at each phase during the nanoimprinting process. Figures 5, 6 and 7 depicts the change in the density of substrate atoms at different imprint depths. The density of gold at 293 K is 19.32 g/cm³. The atomic mass of gold is 196.966 g/mol. After transforming the density using the Avogadro's constant the atomic density of gold is 0.06 atoms/Å³.

Figure 5 describes the density profile of gold substrate for 500,000 time step simulation. At initial position and temp ramp-up phase, the density of substrate stayed constant at 0.06 atoms/Å³ which is a normal density of the gold substrate. As the mold loaded into the substrate the density of substrate atoms increased. When mold reached 500,000 steps (i.e. 1.7 nm into the substrate), density reached 0.077 atoms/Å³ which was the highest density. This increase occurred as the gold atoms clustered around the mold tooth. This cluster of gold atoms was seen in the region of actual deformation from 1 nm to 2 nm. However, the density in the rest of the substrate region remained normal. During the mold holding, temp ramp down and relaxation phases the recrystallization of atoms occurred after the plastic deformation which led to the lowering of the material density. Finally, after mold unloading, the density of the gold substrate remained at 0.067 atoms/Å³.

Figure 6 represents the density profile of the substrate after 1 million time steps (i.e. 3.9 nm deep). The highest density was 0.09 atoms/Å³ at the end of mold loading phase. This increase in density was attributed to the physical deformation of substrate due to the compressive forces subjected by the mold. The density was highest between 3 nm to 4 nm, which was the final depth of the mold after 1 million time steps. In the remaining phases, the substrate atoms recrystallized resulting in lowering the density to 0.070 atoms/Å³ in the region of deformation. The density in rest of the substrate was normal.

Figure 7 illustrates the density profile for the 1.5 million time steps (i.e. 6.5 nm deep) simulation. After the mold loading phase, the density of substrate was 0.094 atoms/Å³. This was the highest density in the region of deformation from 6 nm to 7 nm. During the subsequent phases of the process, the density of substrate atoms decreased slowly due to the recrystallization of atoms after the imprinting. At the end of mold unloading phase, the density of substrate atoms remained at 0.075 atoms/Å³.

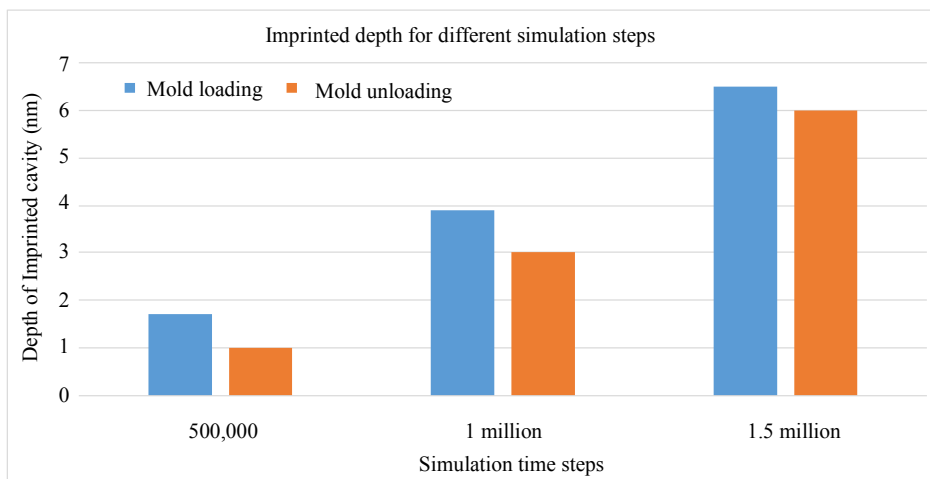


Fig. 4: Imprinted cavity depth vs simulation time steps

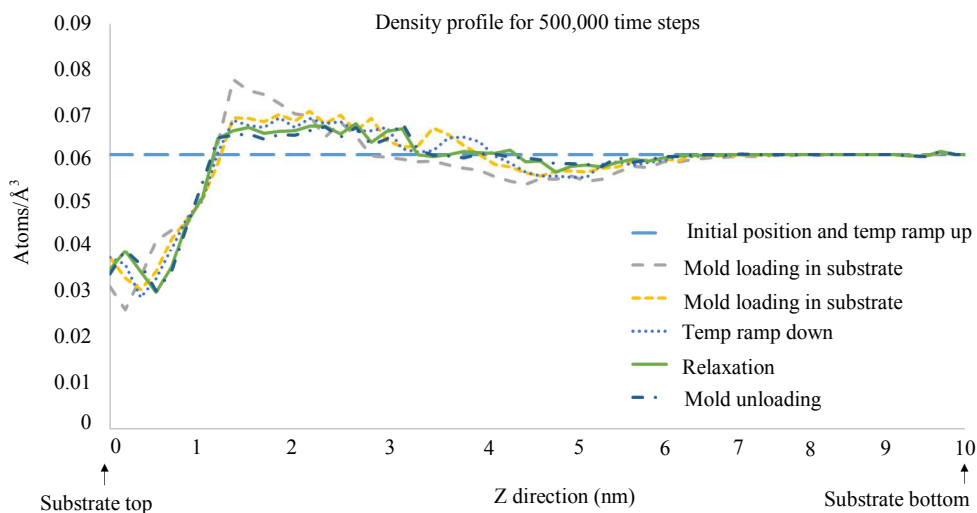


Fig. 5: Density profile of substrate after 500,000 time steps

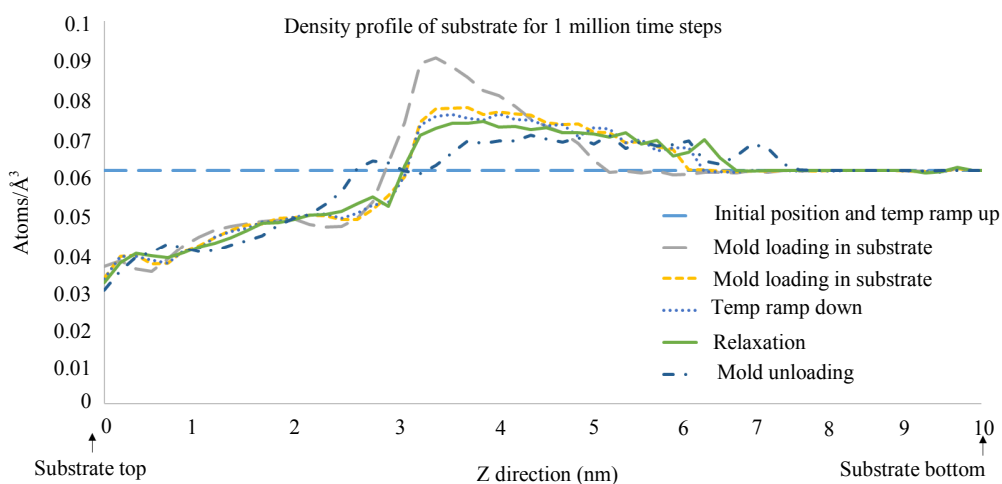


Fig. 6: Density profile of after 1 million time steps

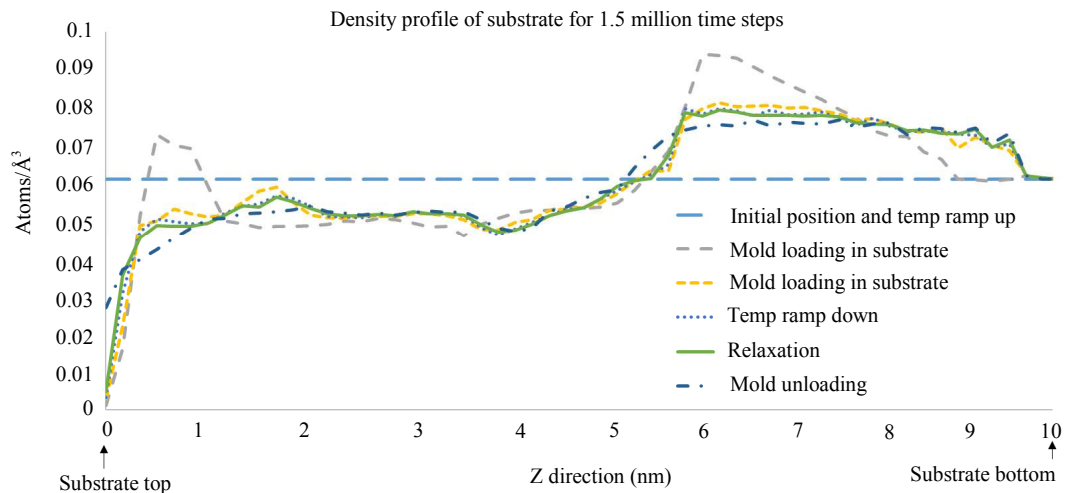


Fig. 7: Density profile of substrate after 1.5 million time steps

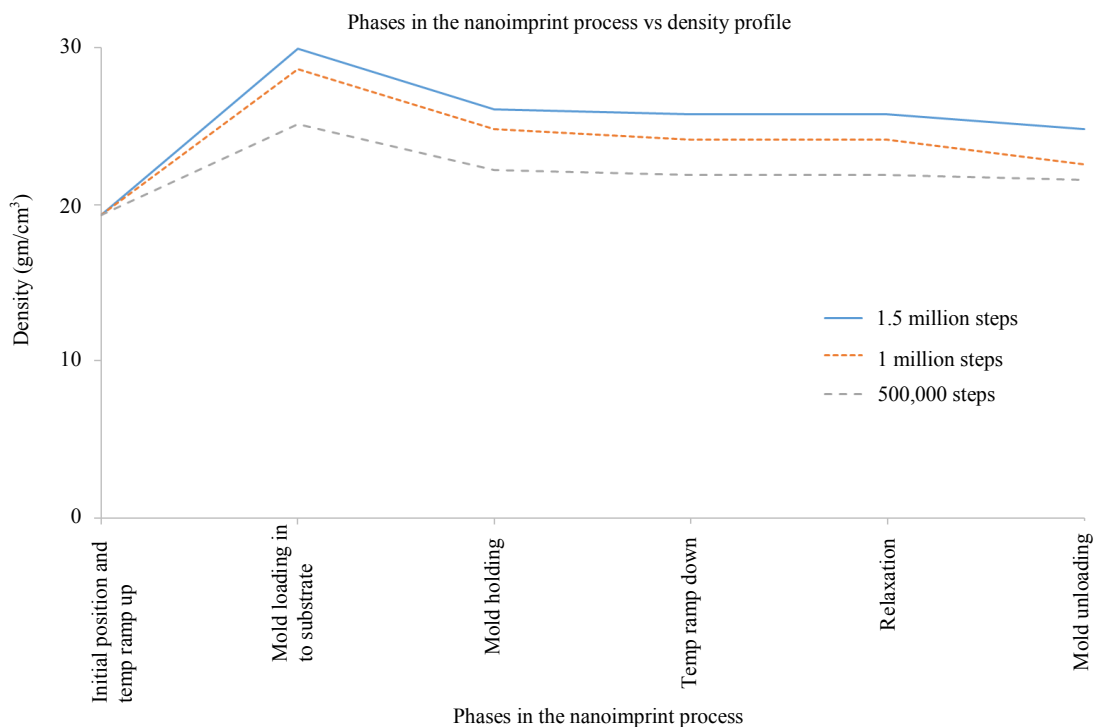


Fig. 8: Phases in the nanoimprint process vs density profile

Figure 8 shows the variation in the density of substrate at each phase of mold loading for different imprint depths. For the 1.5 million time step simulation the density during the mold loading reached to 29.95 g/cm^3 which was 1.55 times the normal density. Similarly, for 1 million time steps and 500,000 time steps the density during mold loading increased by 1.50 and 1.32 times the normal density, respectively. The MD simulations revealed that as the number of steps (i.e. imprint depth) increased the density of atoms in the substrate increased. In addition, the peak density was

attained after the mold loading phase followed by subsequent lowering of density during the recrystallization and unloading phases of the imprinting process. The variations in the density profile were observed for different imprinting depths.

Conclusion

This paper investigates the physical deformation of the gold substrate by a silicon mold during the nanoimprinting process. The silicon mold was loaded for

500,000, 1 million and 1.5 million time steps within the gold substrate. A spring back phenomenon was observed and validated by measuring the imprinted cavity for all the three imprint depths. The simulations with 1.5 million steps had the narrowest width of 3.1 nm which indicated that as the mold is loaded deep into the substrate the spring back effect was prominent. The density of atoms in the region close to the mold tooth was the highest as compared to the outer regions of the substrate. In addition, it was revealed that the density of atoms in the gold substrate was highest during the mold loading phase of the nanoimprinting process. Variations in the density profile were observed for different imprinting stages. Recrystallization of substrate molecules during mold holding and subsequent cooling phase resulted in lowering of substrate density. Substrate molecules were dislodged from their imprint position during mold unloading due to higher adhesion energies between the Si mold and Au substrate. This research lays the foundation for identifying the relationship between mold geometry and imprinted cavity for successful pattern replication.

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Author's Contributions

Abhaysinh Gaikwad and Salil Desai: Performed simulation work and conducted analysis of the research. All authors contributed to the writing of the manuscript.

Ethics

The authors declare that there are no ethical issues that could arise after the publication of this study.

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