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Annealing recovery of nanoscale silicon surface damage caused by Ga focused ion beam

Y.J. Xiao, F.Z. Fang*, Z.W. Xu**, X.T. Hu

State Key Laboratory of Precision Measuring Technology & Instruments, Centre of MicroNano Manufacturing Technology, Tianjin University, 300072, China

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ABSTRACT

In this paper, molecular dynamics method with the Tersoff–ZBL combined interatomic potential was adopted to study the dynamics of focused ion beam (FIB) milling and subsequent annealing. The Ga FIB induced damage and its recovery mechanism during subsequent annealing process were investigated in nanoscale time and space. To investigate the nanoscale damage during FIB milling with the ion energy of 0.5 keV, 1 keV and 2 keV, radial distribution function, bond length distribution, bond angle distribution, and common neighbour analysis (CNA) were calculated and analyzed under various ion doses. FIB irradiated silicon substrate with ion dose of 2×10^{14} ions/cm^2 was annealed at various annealing temperatures from 1400 K to 2400 K. Molecular dynamics simulation illustrated that as *a*-Si region was surrounded by *c*-Si after implantation, the recrystallization lead to a *c*-Si regrowth processes both from bottom towards top surface and from periphery to centre. The damage area profiles by CNA represented a shortest recovery time of 2.0 ns at 2200 K. Both melting on the top surface and recrystallization at crystalline/amorphous interface have existed as annealing at 2400 K, which is near the melting point. Ga migrated together and moved towards the surface with the *a*-Si/*c*-Si interface.

1. Introduction

With a trend of increasing miniaturization of devices and components in recent year, focused ion beam (FIB) has become an indispensable tools for abundant applications in the field of micro/nano-manufacture, including transmission electron microscopy (TEM) sample preparation [1,2], semiconductor devices failure analysis [3], 3-dimensional structure [4], patterning [5,6] and surface characterization or secondary electron imaging [7,8]. The major developments of FIB instrument used liquid metal ion source (LIMS) were during the late 1970s and the early 1980s, since the first high brightness gallium (Ga) LIMS had been invented by Krohn and Ringo from American National Laboratory Argonne in 1975 [9]. Until now, the Ga LIMS is still wildly available profit from its low melting point (29.8 °C) [10], low vapour pressure (<10–12 Torr) and excellent oxidation stability [11].

It is unable to avoid the formation of amorphous layers during FIB milling. As the ion dose increases, the ion collisions can cause point-like damage, defect clusters, amorphous pockets; and finally form continuous amorphous layers [12]. The ion-implanted impurity (Ga^+ ions) can also form a contamination layer on the target [13]. The alternation of surface micro-structure and chemical composition would degrade the optical [14–16], electrical [17,18] and mechanical [19] properties of devices. The TEM resolution is also reduced by the damage layers on the two faces of TEM samples [20].

To study the dynamics of solids processing by energetic particles, molecular dynamics (MD) simulation based on empirical potential has been employed in recent decades. Caturla et al. employed molecular dynamics to study cascades of different ion mass and energy in silicon after single-ion implanted [21]. Krasheninnikov et al. built molecular dynamics moulds of ion impacts on nanotubes to investigate the formation of ion-irradiation-induced defects [22]. The processes of clusters and molecular implantation to silicon have also been investigated using molecular dynamics simulations [23,24]. A few MD calculations are focused on the interactions between focused ion beams especial Ga^+ ions and target atoms. Russo et al. performed MD simulations of Ga^+ FIB-milling with 2 keV and 30 keV energies to examine the extent of lateral damage, sputtering and displacement of target atoms [25]. Pastewka et al. calculated surface amorphization, sputter rate, and intrinsic stresses of silicon during FIB [26].

In order to remove the strain and recrystallize the amorphous pockets, some researchers have tried a post repair process, i.e.,

* Corresponding author at: Building 5, No. 108, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, China. Tel.: +86 22 27407503; fax: +86 22 59813864.
** Corresponding author at: Building 5, No. 108, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, China. Tel.: +86 022 27403753.
E-mail addresses: fzfang@gmail.com (F.Z. Fang), zongweixu@163.com (Z.W. Xu).

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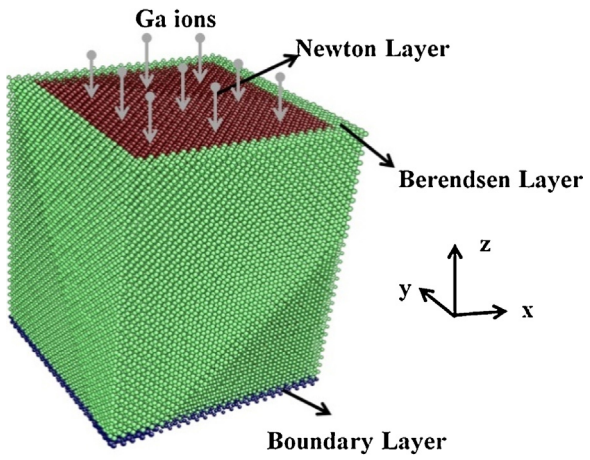

Fig. 1. The MD simulation mould for FIB milling.

annealing to limit these influences [15,18,27]. The transmission performance and optical quality of micro or nano-photonic devices, which is declined significantly being induced in silicon by etching with a focused-ion beam [14,15], improved after subsequent annealing [15]. Noise of FIB milled device significantly reduced after a low temperature annealing (200–600 °C) and cross phase shifts also increased [18,28].

Crystalline silicon (*c*-Si) has been chosen to investigate the system due to its contribution in the semiconductor and MEMS industry. In our previous work [29], the evolution of Si surface after FIB milling and subsequent annealing is studied. Gallium migrated to clusters in the top of amorphous Si (*a*-Si) layer, which was transformed from *c*-Si after large dose implantation. Ga impurity was completely segregated from Si after an annealing at 800 °C for 30 min, but the Si surface was left quite rough. Recently, array holes fabricated by the implantation of Ga ions were used to control quantum dot nucleation at >500 °C [30–32].

Fundamental researches on focused ion beam (FIB) induced damage play an important role in FIB nano-manufacturing and its application. However, either conducting actual experiments or characterizating sample performance at the nanoscale is a rather difficult task. Due to lack of online testing approaches in FIB machining, available experimental studies acquire rather fragmentary data. In consequence of this, MD simulation is chosen to obtain indpeth studies of the Ga^+ ions and materials the dynamics during FIB-milling and subsequent annealing in this paper. In this paper, the evolution of a hole formed by implantation in subsequent annealing is studied. Besides the ion implantation damage and recrystallization of Si, we have focused on the diffusion and movement of gallium during implantation and annealing in this study.

2. Computational details

2.1. MD mould for ion implantation

Fig. 1 shows the 3D molecular dynamics simulation mould for Ga^+ focused ion beam milling. The target material is monocrystalline silicon with a size of 13 nm × 13 nm × 16.3 nm, including 138,240 Si atoms. The implantation area for a hole is 10 nm × 10 nm. The main atoms interacting with Ga^+ ions, which lay in the middle of the simulation box, belonged to the Newton layer. Their motion obeyed the classical Newton's second law. The Berendsen layer performed a Berendsen thermostat [33], and it would keep at a constant temperature of 293 K to imitate the heat dissipation. It contains several layers of atoms around the Newton layer except the top side. Atoms at the bottom Si (0 0 1) plane were froze during the whole process of ion implanted, for the purpose of imitating the boundary of Si, which supplied the simple avoidance of the translation of the simulation box along the ions implanting direction. The top-most Si (0 0 1) plane was free, i.e., the sputtered particles were removed from the system when they crossed the top of the simulation box. The [1 0 0] and [0 1 0] direction were applied periodic boundary conditions for an infinite plate.

The simulation started from an perfect initial slab of *c*-Si. Firstly, the system was equilibrated at 293 K for 50,000 iterations after initiated by assigning a Boltzmann distribution of velocities at 293 K. Then, a total of 200 Ga ions implanted to the silicon (0 0 1) one by one with the incident angle of 0°, which is perpendicular to the surface of Si. To study the influence of ion energy, the Si was impacted by Ga ions with the energy of 0.5 keV, 1 keV and 2 keV, respectively. The ions implanted to Si with a height of 1 nm above the bottom. The initial potential energy of Ga^+ is ignored, thus the initial kinetic energy of Ga ions is corresponding to the implantation energy. During the cascades in silicon atoms, the velocity of Ga ions greatly changes from 7.44 Å/fs (when the ion energy equal to 2 keV) to less than 0.02 Å/fs. Taking into account the computational limitations and simulation accuracy, the MD time-step was reset in a range of 0.002–1 fs during calculation, making sure no atom moves further than 0.02 Å per iteration [34]. The system was relaxed for 50,000 iterations after per Ga atom implanted, after which the whole slab would reach ~293 K. A Ga implanted rate of ~50 ps/ion, which decreases with the increasing of the initial ion energy, implies a flux of $\sim 2 \times 10^{22}\ cm^{-2}\ s^{-1}$. The molecular dynamics simulations were carried on LAMMPS programme code [35]. Structures were visualized using VMD (visual molecular dynamics) software [36] or AtomEye software [37].

The forces and energies in the system during ion collisions were briefly depicted by the empirical potential functions. A short range core repulsive ZBL potential [38] was used to describe the binary collision between Ga and Si at short inter-atomic distances. Considering the long range interactions among silicon atoms in the substrate for covalent systems, Tersoff potential [39] was splined smoothly to ZBL potential:

$$E = \frac{1}{2}\sum_i \sum_{j=i} V_{ij} \tag{1}$$

$$V_{ij} = (1 - f_F(r_{ij}))V_{ij}^{ZBL} + f_F(r_{ij})V_{ij}^{Tersoff} \tag{2}$$

$$f_F(r_{ij}) = \frac{1}{1 + e^{-A_F(r_{ij} - r_c)}} \tag{3}$$

where the V_{ij}^{ZBL} and $V_{ij}^{Tersoff}$ indicate ZBL portion and Tersoff portion, respectively. The parameters of A_F and r_c are used to adjust f_F : A_F controls how "sharp" the transition is between the ZBL portion and Tersoff portion, and r_c is essentially the cutoff for the ZBL potential. r_{ij} is equal to the distance between atoms *i* and *j*. The parameters of Tersoff potential for Si—Si and Ga—Ga interaction were given in Ref. [39] and Ref. [40], respectively.

2.2. MD simulation of annealing

After implantation with 200 Ga ions of 1 keV energy, the kinetics of the recrystallization process is studied. The system was annealed at different temperatures (1400 K, 1600 K, 1800 K, 2000 K, 2200 K and 2400 K) in vapour. Nose–Hoover thermostat (NPT ensemble) was used in the annealing system. Periodic boundary conditions were applied at all six faces. To save computational effort, the lower crystalline layer was removed before annealing, and only the upper amorphous layer with the thickness of 65.16 Å underwent thermal