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Molecular dynamics simulations of the sputtering process of silicon and the homoepitaxial growth of a Si coating on silicon

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ABSTRACT

Molecular dynamics simulations of the sputtering process of silicon by Ar atoms in the low energy range, 20 eV–1000 eV, were performed using the IMD software package and the commercial software Materials Explorer 4.0 from Fujitsu Ltd. with the combination of the Tersoff potential and the Ziegler–Biersack–Littmrk (ZBL) potential in order to get more insight into the sputter process itself and to extract data comparable to experiments. The analysis of the sputter yield as a function of argon impact energy, surface impact coordinate and of crystal orientation was performed. These simulation results were compared with experimental values as determined by Ar ion etching in a microwave plasma and measurement of the etch depth and etch time. A good agreement between experiments and simulations was found. Physical parameters such as binding energy of the Si (0 0 1) surface, vacancy energy and vacancy migration energy were also determined in order to explain the simulation results of the sputter process. Finally, the coating process of a silicon substrate by Si atoms was simulated using the Si sputter results as input parameters.

1. Introduction

Classical molecular dynamics (MD) has proved itself as a well suited method for the simulation of structural and mechanical properties of materials at the atomic scale, in the case of large systems (number of atoms greater than 1000). Within this method, atoms of a solid are regarded as point particles, interacting by classical potential functions. Newton equations of motion are numerically integrated, with the possibility to take into account certain boundary conditions, e.g. external forces or deformations and to use various thermodynamic ensembles, such as the canonical NVT ensemble (i.e. a system with a constant volume in contact with a heat bath of constant temperature). From the data calculated in the MD simulation, energies, stresses, distortions and elastic constants can be determined locally. For the simulation of covalent solids, as in the case of silicon, many-body potentials such as the Tersoff potential are required, allowing the representation of angle dependent bonds [1].

As it will be shown in this work, physical parameters such as surface binding energy, vacancy energy and vacancy migration energy of silicon can be well reproduced using the Tersoff potential. In the case of back sputtering, which is considered as a removal of target atoms by ion bombardment, an additional potential is introduced, describing the interaction with bombarding atoms; in our case, argon. Such potential is the ZBL-potential, developed by Ziegler et al. [2]. Sputter yield is defined as the number of target atoms removed per incident ion.

MD simulations of sputter processes are especially suited for lower impact energies, below 1 keV, because at higher energies the binary collision approximation as implemented e.g. in TRIM [3], is more appropriate due to the spatial separation of the single collision cascades. In [4] Aoki et al. compared the sputter yields of Si determined by MD simulations for bombardment of Ar ions in the energy range between 100 eV and 500 eV with MC simulations using the T-DYN code. They reported a good agreement between both methods in this energy range; however, they made no comparison with experimental data. In 1998, Kubota et al. calculated the sputter yield of Si for bombardment with Ar by MD simulations in the low energy range of 25–200 eV and compared them to available experimental data [5]. Their study was in very a good agreement with the experimental yields of Balooch et al. [6] and MD studies of Barone and Graves [7]. Moreover, their calculated yield corresponded well to the yield estimates of Zalm [8]. Kang et al. measured and simulated sputter yields of Si for the high energy range of 3–10 keV [9]. In 2002 Ecke et al. compared the experimental sputter yields of Si for bombardment of Ar ions in the energy range between 0.5 and 5 keV under a 60° angle sputtering with MC simulations using the programs TRIM and T-DYN. They reported that the differences between the results of the simulation programs were sometimes greater than the difference of the individual simulation data from the experimentally measured

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sputter yields [10]. Moreover they compared their experimental results with data from Kirschner and Etzkorn [11] and found out that their measured values seemed to be too high. Zalm measured the sputter yield of Si for Ar in the energy range of 0.2–20 keV [12] and he found a very good agreement with the Siegmund sputter theory [13]. The evaluation of the existing data shows that there is still a gap in the energy range between 20 eV and 1 keV where either experimental or simulation data are missing. Therefore, in this work, MD simulations of the sputtering process of silicon by Ar ions in the energy range, 20–1 keV, were performed using the IMD software package [14,15] and a commercial software Materials Explorer 4.0 from Fujitsu Ltd. and the simulations were compared with experimental data as determined by Ar ion etching in a microwave plasma.

Finally, using the simulation results of the sputtering of Si, the coating process of a silicon substrate by Si atoms was simulated. By this, important correlations between the process parameters and the film microstructure, constitution and properties could be derived. In 1987 Gawlinski and Gunton modelled the molecular beam epitaxy deposition of a Si film onto a Si (1 0 0) surface by the MD method with special emphasis on the correlation between the substrate temperature and the morphology of the growing film [16]. They found a critical epitaxial transition temperature being 42.5% of T_{melt}, i.e. 717 K. Below this temperature only amorphous films could be deposited, while the formation of crystalline films required $T > T_{epitaxial}$. However, in experiments, it has been shown that nanocrystalline Si films can be sputtered onto a Si wafer even at room temperature [17]. Therefore the critical epitaxial transition temperature will be reinvestigated and complementary to their study, the influence of further parameters such as the substrate orientation and impact energies of adatoms will be shown in this work.

2. Computational methods

For the calculation of the surface binding energy, vacancy energy and vacancy migration energy a cubic Si specimen consisting of 2744 atoms was used. Periodic boundary conditions in the lateral (***x***,***y***) direction were applied in order to mimic a semi-infinite surface and remove edge-effects while using free boundary conditions in the ***z***-direction. Free boundary conditions in the ***z***-direction were used for the calculation of the surface binding energy, while periodic boundary conditions in all directions were used for the calculation of vacancy and the migration energy.

Global micro-convergence integrator was chosen as an ensemble: a small initial temperature was set at first; if during the calculation the scalar product of the global force and momentum vectors (containing the force and momentum components of all atoms) was negative (momentum went "uphill" in the potential landscape), all momenta were reseted to zero. This procedure allows the system to relax into potential minimum.

For the calculation of the surface binding energy, one silicon atom on the surface was chosen and moved continuously away from the sample. The movement itself was simulated by fixing the chosen silicon atom at different distances from the surface in the range of $0 < \text{distance} < r_{cut}$, with r_{cut} being the cut off radius of the Tersoff potential. For each distance, the average potential energy of the system was calculated.

The remaining atoms were treated in two different ways: in one case, all other atoms were also held fixed; in this case, the removal of one silicon atom from the surface lead to the absolute value of the surface binding energy. In the second case, only the bottom layer atoms were held fixed, hereby preventing the unphysical centre of mass drift, crystal surface recombination around the vacancy site was still allowed, therefore reducing the effective surface binding energy by 0.3 eV.

The calculation of the vacancy energy was performed by comparing two samples of the same size, one with and one without a vacancy site inside.

As it will be shown later in this work, silicon bombardment by Ar causes shock waves inside the crystal lattice, causing not only the back sputter yield but also forward sputter yield, represented by the amount of silicon atoms pushed in the negative ***z***-direction per incident Ar ion. Important for the quantification of this process is the understanding of the migration of silicon inside the silicon crystal lattice. In this work the migration energy was defined as the energy needed for one silicon atom to move from its original site into the nearest vacancy.

From the simulation stand point, the calculation of the migration energy prerequires the combination of the two methods described above. At first, a single vacancy site was produced inside the crystal, relaxing the sample around it. In the next step, one of the four neighbouring silicon atoms was chosen and moved on the direct path from its original site towards the vacancy. Due to the fact that after the movement inside the vacancy, the chosen atom produces a vacancy at its original site, the energy level of both the start and end point must be the same. As in the case for the surface binding energy, the actual movement was represented by fixing the chosen atom at discrete points along the original atom site-vacancy connection line, while calculating the average potential energy of the system.

In analogy to the calculation of the surface binding energy, for the calculation of the migration energy, two cases had to be distinguished. In the first case, all atoms of the sample were fixed defining migration energy only trough the movement of the chosen Si atom. In the other case, the relaxation of all other atoms, especially those neighbouring the vacancy site, was allowed, leading to migration energy being set together from the local potential energy of the moving Si atom and the local potential energies of the recombining atoms around the vacancy site. The latter case lead to lowering of the absolute value of the migration energy, as well as to stable interstitial states.

The calculated potential energies were then set as function of the position of the selected silicon atom, resulting into two potential barriers diagrams.

2.1. Simulation of the sputtering process

The sputtering process was simulated using both the commercial software package Materials Explorer 4.0 (ME) (Fujitsu Ltd.) and the program package IMD (ITAP Molecular Dynamics) [14,15] to study the energy dependence of the sputter yield. The chosen Si cell sizes were $6 \times 6 \times 8$ units cells (2304 atoms, energy range 20–500 eV) for the ME simulations, and $10 \times 10 \times 20$ unit cells (16,000 atoms, energy range 20 eV–1 keV) for the IMD simulations. The dimensions of the simulation box were chosen carefully, bearing in mind the intended energy maximum of the Ar ion and therefore preventing the case of an Ar ion penetration through the sample during the simulation. At first, the sample was heated to 700 K by a NPT ensemble using the Nose–Hoover thermostat for temperature control and isotropic volume scaling for the pressure control. Integration time step of 1 fs was chosen, small enough to resolve crystal lattice oscillations at this temperature. The sputter process itself was simulated for an incident angle of 0° using three different methods with 0.1 fs as a time step, which was needed to effectively resolve the Ar movement at 1 keV as well as the movement of target Si atoms during the collisions. For the Ar impact energy between 20 eV and 100 eV, 10 eV steps were used in order to determine the exact threshold energy, between 100 eV and 1 keV, step size was increased to 50 eV.

In the first IMD method (IMD 1), well defined surface impact coordinates presented in Fig. 1 on the Si (1 0 0) were chosen, taking