EFFECTS ON ENERGETIC IMPACT OF ATOMIC CLUSTERS WITH SURFACES

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A brief state-of-the-art review in the field of cluster ion interaction with surface is presented. Cluster beams are efficient tools for manipulating agglomerates of atoms providing control over the synthesis as well as modification of surfaces on the nm-scale. The application of cluster beams for technological purposes requires knowledge of the physics of cluster-surface impact. This has some significant differences compared to monomer ion – surface interactions. The main effects of cluster-surface collisions are discussed. Recent results obtained in experiments on silicon surface nanostructuring using keV-energy implantation of inert gas cluster ions are presented and compared with molecular dynamics (MD) simulations.

Introduction

Ion beam technologies have attained an advanced stage of development. However, nowadays fabrication of nanometre-scale structures needs much more controllable and versatile methods on an atomistic scale. Cluster beams can be tools for manipulating agglomerates of atoms providing the synthesis and modification of structures on the nm-scale. Atomic (or molecular) clusters are aggregates of a few up to tens of thousands of atoms (or molecules) that show properties intermediate between those of individual atoms (or molecules), with discrete energy states, and bulk matter characterised by continua or bands of states.

In the last two decades there has been considerable progress in cluster science as well as in experimental techniques that nowadays provide well-controlled beams of clusters of various species [1]. In particular, one can control the cluster (nanoparticle) composition and size, its impact energy and, to a certain extent, the spatial distribution of the deposited nanoparticles on a surface, for example, by preliminary processing or functionalisation [2,3]. Finite size (quantum) effects lead to electronic, optical, magnetic and other properties that are quite different from those of molecules or condensed matter and that are of great interest for practical applications in nanotechnology [4-6]. With clusters consisting of up to thousands of atoms it is possible to transport and locally deposit a large amount of material, providing an advanced method for growth of thin films which can be either porous or very compact and smooth depending on the energy regime used for cluster impact [7,8]. Low-energy cluster implantation is found to be an efficient tool for doping of shallow layers with suppression of dopant diffusion during post-implantation annealing [9]. Recently, this regime of low-energy cluster implantation was further developed into so-called infusion doping allowing ultrashallow and high-concentration doping as well as monolayer deposition control [10]. Cluster beams are recognised to be very efficient tools for processing surfaces (dry etching and cleaning) or smoothing [11]. These approaches are already utilised for manufacturing of surfaces with low roughness for the fabrication of new generations of semiconductor devices and photonic structures [12].

The application of cluster beams requires knowledge of the physics of cluster-surface impact. However, there are still a lot of fundamental aspects that have to be studied to provide successful material modification using cluster beams.

Energetic cluster-surface interaction: main effects

Cluster-surface interactions can be divided into two main categories: *low-energy deposition* and *energetic impact* (Fig. 1) [13]. There is no precise dividing line on the energy scale for those two cases. However, one can consider a process as low-energy when the energy per atom of the accelerated cluster is below the binding energy of constituents in the cluster (so-called soft landing). The clusters preserve their composition but the structure can be distorted. One of the problems of soft landing, in terms of some practical applications, is the surface diffusive mobility of the deposited clusters, leading to either the growth of larger particles or cluster coalescence.

In this paper we mainly discuss the other regime, i.e. when the energy per constituent atom given to the cluster by the acceleration (hereinafter cluster energy) is greater than the binding energy of the cluster constituents. This regime is used in applications requiring shallow implantation, surface smoothing or nanostructuring.

Under energetic impact the cluster loses its structure. The higher the cluster energy, the more the cluster is deformed on surface impact. However, the cluster constituents penetrate into the substrate only if their energy is higher than the penetration threshold energy which depends on the cluster species and substrate material and can vary from a few to a few tens of eV per atom. When the energetic cluster disrupts the substrate lattice, such that a few atoms from the surface layer are displaced and some of the clusters atoms implant, it becomes pinned and can be used for immobilisation of sequentially deposited objects [14].

Due to the large size and weak bonding between atoms, cluster implantation is fundamentally different from that of monomer ion implantation. Clusters generate multiple-collision effects during the penetration into the target. One more peculiarity of the cluster-solid interaction is nonlinearity, which arises from the fact that the cluster atoms influence each other during the penetration into the target and thus the environment in the material is different for each atom or ion of the cluster. From MD and Monte Carlo simulations, it was suggested that a so-called

"clearing-the-way effect", where the "front" atoms of the cluster push target atoms out of the way, could take place. Heavier ions would thus be expected to cause more clearing of "light" targets [15]. As a result of the "clearing-the-way" the stopping power of the cluster is reduced and the projected range is increased. This effect was experimentally confirmed [16]. A closely-related problem is the radiation damage in the target. MD simulations of Ar_n clusters impacting on Si showed that a similar damage region is formed by both large (hundreds of atoms) and small (tens of atoms) clusters if the total implantation energy (energy per cluster) is the same [17]. Unfortunately, this question has not been extensively studied so far.

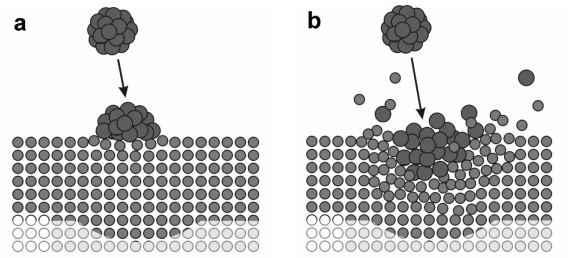

Fig. 1. Schematic pictures of (a) cluster low-energy deposition and (b) energetic impact

Although one would expect nuclear stopping to dominate for clusters, it was found that electronic stopping becomes important due to a coherent interaction of the cluster with the medium. This is called the vicinage effect. The electron vicinage effect leads to enhancement of the cluster stopping power (energy loss) compared to monomers as a result of interference in the excitation of target electrons by the simultaneous interactions with a few ions (cluster constituents or recoils). This effect is found to be important mainly for very high implantation energies (MeV-GeV range) [18].

Considerable attention has been given to the erosion of surfaces under the impact of energetic particles. A very high sputtering yield induced by cluster bombardment has been theoretically predicted and experimentally observed on various types of surfaces [11, 19]. The sputtering is caused by violent impact, semi-spherical shock wave and crater formation. As a result of high-energy transfer to the target the atomic arrangement in the crater region becomes highly disordered. These atoms possess high kinetic energy and a large fraction of them obtain moments directed away from the surface. According to MD simulations, the driving force for the smoothing mechanism can be thought of as a high non-equilibrium surface diffusivity of target atoms in the rim of the crater [20]. The rough surface can be modelled as a sequence of hills and valleys. The simulations showed that if the cluster hits the central part of a hill the material is efficiently removed. A valley impact leads to much lower sputtering yield. When the cluster impacts a slope, a downhill particle current transferring the material into the valley is induced [20]. Thus, the height difference between hills and valleys is decreased and the surface becomes smoother.

Energetic impact of a cluster creates a violent interaction between atoms in the central zone where equivalent temperature and pressure may reach 10^5 K and 10^{10} Pa, respectively [21], leading to a number of effects: thermal spike, local melting and viscous flow that are affected by the shock wave, elastic rebound etc. Some of the consequences of these effects are discussed below.

Nano-modification on cluster impact

The effect of the high density of the energy transferred from cluster to the target at the beginning of impact can be compared to some extent with a nanoscopic analogue of a meteorite-planet collision that typically results in crater formation [21]. Along with craters, hillocks (nm-size protrusions) were found experimentally [21,22]. They typically have heights of a few nm. The basal diameter varies between 10-30 nm. In recent experiments it was shown that hillocks can be located in the craters forming so-called complex craters (Fig. 2), i.e. hillock surrounded by a rim [23]. Detailed experimental studies have provided data for a qualitative model of the hillock formation. This model is based on the effect of multiple collisions causing high density of energy deposition via the nuclear stopping mechanism resulting in a local melting of material around the impact spot. Local tensions and elastic rebound lead to viscous flow and expulsion of the molten material forming the hillock. However, the formation of the surrounding rim is questionable because it typically varies between 20-50 nm in diameter for the keV impact energies and cluster sizes of a few tens of atoms [23]. These values are too large for the rim to be just material which is expulsed on the cluster impact. MD simulations predict crater diameter of just a few nm [24] for the same cluster sizes and energies that were used in the experiments. Thus, some other origin for the formation of the surrounding rim should be considered.

Recent MD simulations of keV-energy Ar_{12} cluster collisions with Si demonstrated that the impact leads to the collective movement (oscillations) of the target atoms around the collision cascade on the ps time scale [25]. First, the atoms move downwards and away from the cascade. Then a counter movement occurs. Taking into account that the target material is locally molten, one can infer the existence of a surface wave propagating away from the impact spot. Quenching of this wave may lead to the rim formation. This process should depend on the composition of the layer where the cluster stops. Si wafers typically have a 2-3 nm thick oxide layer on the surface. MD simulations of Ar_{12} cluster impacts with energies of 3-15 keV show that lateral velocities of the target atoms around the collision cascade have a maximum at the depth of ca. 2 nm, i.e. at the interface of SiO_2 and Si [25]. Since these materials have

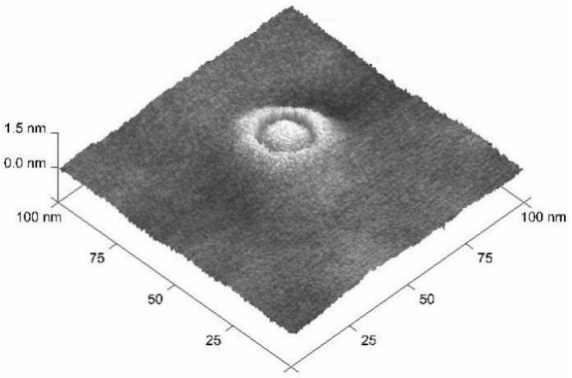

Fig. 2. AFM image of complex crater with diameter of 18 nm on Si surface implanted by 18 keV Ar_{12}^+ cluster ions.

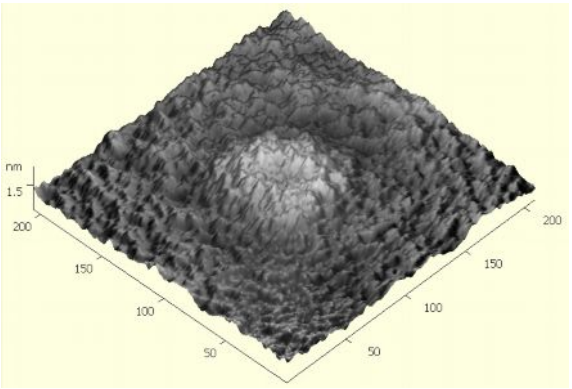

Fig. 3. AFM image of nano-vulcano structure on sputtered Si surface implanted by 3 keV Ar_{43}^+ cluster ions.

different properties, in particular, different melting points, densities and thermal conductivities, the complex crater formation can be affected by the presence or absence of the SiO_2 layer.

To provide evidence for this suggestion, argon cluster ion implantation was carried out for non-sputtered (with the oxide layer) and sputtered (without the oxide layer) Si(111) using CIDA and PU-CLUS facilities [26]. A commercial Ar ion gun (Vacuum Generators) with an energy of 1 keV is used for the sputtering. The implanted surfaces are analysed by a scanning probe microscope Ntegra (NT-MDT) in tapping mode. Ultra sharp DLC cantilevers with a tip curvature radius of 1-3 nm are used.

In the case of 3 keV Ar_{16}^+ cluster ion implantation, the pre-implantation sputtering leads to drastic elimination of the hillock formation compared to the non-sputtered Si. The sputtering not only removes the oxide layer but also radiationally damages and amorphises the thin surface layer of the crystalline Si. This may be the reason for the hillock disappearance. In the case of the same implantation energy but heavier clusters, Ar_{43}, there is also a difference found between the non-sputtered and sputtered samples. For example, on the sputtered Si there new complex structures appear having the shape of "nano-volcanoes" with heights of 1.0-1.5 nm and basal diameters of 60-80 nm (Fig. 3).

To eliminate the effect of amorphisation originated by the sputtering the next sample was annealed *in situ* after the sputtering at a temperature of 550 ^oC for 15 min. This annealing should lead to the recrystallisation of the amorphous layer. This sample was implanted by 15 keV Ar_{43}^+ cluster ions. On the non-sputtered sample both complex and simple craters are found similar to the case of 15 keV Ar_{54}^+ cluster ion implantation reported earlier [23] while on the sputtered and annealed sample predominantly hillocks (without surrounding rim) with heights of 1.5-2.0 nm and basal diameters of 15-20 nm are observed. These results indicate the important role of the surface oxide layer in the formation of nanostructures on cluster implantation of silicon. However, further detailed study of these phenomena is needed.

Conclusion

The study of the effects occurring on cluster-surface impact is considered to be very important for the development of fundamental aspects of atomic and material physics as well as for a wide range of practical applications of cluster ion beams in nanoscience and nanotechnology.

A recent series of experiments together with MD simulations is helping to provide detailed understanding of the processes occurring on energetic cluster-surface impact, in particular, on the role of surface composition and structure that is of significant importance for material modification on the nano-scale.

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