Computer simulation of the single crystal surface modification and analysis at grazing low-energy ion bombardment

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Abstract.

The specific peculiarities of 0.5-10 keV Ne⁺, Ar⁺, Kr⁺, Be⁺ and Se⁺ ions scattering, sputtering and implantation processes at grazing ion bombardment of GaAs (001), Si(001), SiC(001) and Cu(100) surfaces and their possible application for the surface modification and analysis have been studied by computer simulation. Sputtering yields in the primary knock-on recoil atoms regime versus the initial energy of incident ions (E₀ = 0.5-5 keV) and angle of incidence (ψ = 0-30°) counted from a target surface have been calculated. The colliding particles mass ratio influence on the energy losses of scattering particles, sputtering yields and near-surface depth distributions of implanted particles is established. It was shown that in the case of grazing ion bombardment the layer-by-layer sputtering is possible and its optimum are observed within the small angle range of the glancing angles near the threshold sputtering angle. Comparative studies of layer-by-layer sputtering for Si(001) and SiC(001) surfaces versus the initial energy of incident ions as well as an effective sputtering and sputtering threshold are discussed.

Introduction

The ion scattering, sputtering and implantation processes has been the subject of both scientific investigations for a long time and recent rapid developing micro- and nanotechnologies. Processes such as plasma etching and sputter deposition that involve ion bombardment at relatively low (~ 100 eV) ion energies are widely used in semiconductor processing. However, using glancing-angle ion bombardment for surface modification rather than conventional near-normal incidence ions allows expanding the energy range up to ~ 10 keV and has the advantages of reducing damage (such as crater formation) and preferentially removing surface asperities leading to flat surfaces. This is due to the peculiarities of sputtering processes at grazing incidence [1].

Si and SiC crystals have a great importance because of their use in semiconductor technologies. Especially, silicon carbide exhibits a large band gap, a higher break down field, a higher thermal conductivity, and a higher saturation velocity, compared to widely used silicon. Besides, SiC is a promising shielding material in nuclear fusion systems such as limiters in Tokamak devices, where the surface erosion is also important [2, 3].

In [4] atomically clean and flat Si(100) surfaces suitable for nanoscale device fabrication were prepared by wet-chemical etching followed by 0.3-1.5 keV Ar ion sputtering. It was found that wet-chemical etching alone cannot produce a clean and flat Si(100) surface which can be achieved by subsequent 300 eV Ar ion sputtering at room temperature followed by a 700 °C annealing. Application of grazing angles of incidence of ions on the solid surface opens new perspectives in the investigation of...
composition, structure and topography of real surfaces and their modification and polishing by ion beams. Sputtering yields of crystalline silicon carbide and silicon have been experimentally determined and results have been compared with Monte Carlo simulations for Ne\(^+\), Ar\(^+\) and Xe\(^+\) ion bombardment in the energy range of 0.5-5 keV under 60° sputtering with respect to the surface normal [5]. The simulation results depend strongly on the input parameters which are not well known especially for SiC. The TRIM simulation fits the experimental results very well.

The (001) surface of III-Y semiconductors is one of the most widely used semiconductor surfaces in both homo- and hetero-epitaxial growth for the manufacturing of electronic devices. Implantation of Be and Se ions into GaAs allows to make the acceptor and donor impurities and ultra shallow junctions in this semiconductor. The evolution of surface morphology during ion beam erosion of Si(111) at 500 eV Ar\(^+\) ion bombardment (60° from normal, 0.75 mA/cm\(^2\) collimated beam current) was studied over a temperature range of 500-730 °C [6]. Keeping ion flux, incident angle, and energy fixed, it was found that one-dimensional sputter ripples with wave vector oriented perpendicular to the projected ion beam direction form during sputtering at the lower end of the temperature range. For temperatures above approximately 690° C, growth modes both parallel and perpendicular to the projected ion beam direction contribute to the surface morphological evolution.

Thus, though sputtering and surface modifications of single crystals are widely studied, there are not sufficient data in the case of grazing incidence. In the present paper, grazing ion scattering, sputtering and implantation processes on GaAs (001), Si(001), SiC(001) and Cu(100) surfaces at 0.5-10 keV Ne\(^+\), Ar\(^+\), Kr\(^+\), Be\(^+\) and Se\(^+\) ions bombardment have been studied by computer simulation.

**Computer simulation method**

The theoretical investigation of atomic collision processes in crystals caused by ion irradiation is usually done using computer simulation because real physical conditions (e.g. complicated interatomic interaction potential, surfaces, interfaces, defects) can be taken into account much easier than it is possible by using analytical methods. The simulation used in our calculations to construct the trajectories of the ions or projectile scattered by target atoms is based on the binary collision approximation [7] with two main assumptions: (1) only binary collisions of ions with target atoms or between two target atoms are considered; and (2) the path which a projectile goes between collisions is represented by straight-line segments. For the description of the particle interactions the repulsive Ziegler-Biersack-Littmark potential [8] was used. The inelastic energy losses were regarded as local depending on the impact parameter and included into the scattering kinematics.

Sputtering has been simulated in the primary knock-on regime. Only the primary knock-on recoil (PKR) atoms ejected from first, second and third layers have been considered. The presence of planar potential energy barrier on the surface was taken into account. A parallel, uniform, mono-energetic ion beam impinges on an impact area on a surface of a crystal. The angle of incidence of primary ions \(\psi\) was counted from a target surface. It is assumed that the incident beam is of small density, so the ions of the beam do not hit twice at the same place. The number of incident ions is \(4 \times 10^4\). Each new particle is incident on a reset, pure surface. The incident ions and the recoil atoms were followed throughout their slowing-down process until their energy falls below a predetermined energy: 25 eV was used for the incident ions, and the surface binding energy was used for the knock-on atoms. In order to consider simultaneous and nearly simultaneous collisions of a particle with the atoms
of the adjacent chains, the special procedure proposed in [9] was used. The calculations were performed on the crystals comprising up to 120 atomic layers. The simulations were run with the crystal atoms placed stationary at equilibrium lattice sites. The initial energy of incident ions was varied from 0.5 to 10 keV, an angle of incidence \(\psi\) counted from target the surface was 0-30° and an azimuth angle of incidence \(\xi\) realized by rotating the target around its normal and counted from the <100> direction was 0-180°.

**Results and discussion**

In the case of \(\text{Be}^+\) and \(\text{Se}^+\) ions bombarded the GaAs(100) surface at grazing incidence the ions move in the surface semichannels and channels which is parallel to the surface and transfer the small portions of their energy to a great number of atoms which form of channels and semichannels walls. The \(\mu\) values for \(\text{Be}^+\) ions colliding with Ga and As atoms are equal to 7.74 and 8.31, correspondingly, (\(\mu > 1\): direct mass ratio) and for \(\text{Se}^+\) colliding with Ga and As target atoms - to 0.88 and 0.95, correspondingly, (\(\mu < 1\): inverse mass ratio). Here, \(\mu\) is the ratio of target atom mass \(m_2\) to mass of ion \(m_1\). In Figure 1a,b the number of 1keV \(\text{Be}^+\) and \(\text{Se}^+\) ions implanted into GaAs(100) surface versus the incidence angle \(\psi\) for <110> (a) and <\(1\bar{1}0\)> (b) directions are compared.

![Figure 1](image_url)

**Figure 1.** Number of 1keV \(\text{Be}^+\) and \(\text{Se}^+\) ions implanted into GaAs(100) surface versus the incidence angle \(\psi\) for <110> (a) and <\(1\bar{1}0\)> (b) directions

It is established that some difference of these dependencies is explained by different shapes of surface semichannels in these directions. It is clear that at grazing angles smaller than some critical angle, ion implantation does not take place. The value of the critical angle decreases with mass of incident ion decreasing. The inverse mass ratio of colliding particles in case of \(\text{Se}^+\) ions is lead to considerable increase of incidence angle \(\psi_{\text{inSe}}\) from which the ions penetration into GaAs surface layers are begin in comparison with \(\text{Be}^+\) ions (for <110> direction: \(\psi_{\text{inBe}} = 10^\circ\) and \(\psi_{\text{inSe}} = 18^\circ\)).

The number of implanted \(\text{Se}^+\) ions is much greater than the number of \(\text{Be}^+\) ions. At the angles of incidence where the minimum of the dependence is observed (Figure 1a,b) the incident ions are intensively reflected by surface semichannels because of the ion focusing effect [7].
Figure 2 a, b shows implanted depth distributions of 1keV Be\textsuperscript{+} (a) and Se\textsuperscript{+} (b) ions for \textlangle\textbar{1}0\textrangle direction calculated for three incidence angles values. The oscillatory behavior of depth distributions is explained by shape of channel in the \textlangle\textbar{1}0\textrangle direction. At grazing incidence the primary beam ions penetrate in several nearest to surface atomic layers during the process of their movement in channels of low index directions along the surface. Therefore, in this case the main peak of the implanted depth distributions is considerable shallow. Note that 1 layer is 0.136nm. The implanted depth profiles depend on the mass ratio of colliding particles, the crystal orientation and the angle of incidence. At $\psi = 30^\circ$ the depth profile for Se\textsuperscript{+} ions is slightly shifted in the deep layers region (Figure 2,b). The comparison of calculated depth distributions for Be\textsuperscript{+} and Se\textsuperscript{+} ions shows that the range for Se\textsuperscript{+} ions is shallower than that for Be\textsuperscript{+} ions and the half-width of profile for Se\textsuperscript{+} is narrow. Because the small mass and size of Be\textsuperscript{+} ions allows them to penetrate into deep layers region.

In Figure 3 the depth distributions of 5keV Ar\textsuperscript{+} (a) and Kr\textsuperscript{+} (b) ions implanted into Cu(001) \textlangle 110\textrangle surface have been presented for three values of angle of incidence. It is clear that the implanted depth distributions of bombarded particles contain a maximum.

With the angle of incidence $\psi$ increasing the maximum of distribution is slightly shifted on the field of deep layers and a half-width of distribution increases. In a case of Kr ions ($\mu \approx 0.76$: inverse mass ratio of colliding particles) for the incidence angle range up to $\psi=16^\circ$, the main part of implanted ions is arranged in four-fife layers nearest to the surface. The calculated results show that at ion bombardment of Cu(001) surface along a \textlangle 110\textrangle directions the ions are implanted much more deeply due to planar channeling and their depth distributions have not a sharp maximum in the near surface area.
Figure 3. Depth distributions of 5keV (a) Ar$^+$ and (b) Kr$^+$ ions implanted into Cu(001) <110> surface at various grazing angles. Note that 1 layer is 1.81Å.

In Figure 4a,b the angular dependences of the sputtering yield for Si(001) and SiC(001) surfaces subdivided into sputtering by the first three surface layers at 0.5 keV Ne$^+$ ion bombardment are compared. Note, the angle of incidence $\psi$ is counted from the surface [10].

Figure 4. Sputtering yield of Si(001) (a) and SiC(001) (b) versus angle of incidence at Ne$^+$ ion bombardment

It is seen that there is a threshold angle of sputtering in all dependences. At angles of incidence less than the threshold angle the incident ions cannot penetrate into the crystal and cannot eject target atoms. The threshold angle shifts to the lower values of angle of incidence with increasing the energy of incident ions. At $\psi$ large than a threshold angle, with increasing $\psi$ the number of PKR at first rises and achieves its maximum. There is a plateau (shorter for Si and wider for SiC) near the threshold angle because of insufficient ion energy for both long moving ions within surface semichannels and their penetration to deeper layers. With increasing the initial energy this plateau disappears and the sputtering yield decreases at large $\psi$. This decreasing of PKR yields is explained by partial penetration of ions in deeper layers and domination of the cascade sputtering mechanism. It is clear that the relative con-
ttributions of each layer to the total PKR yield strongly depend on the angle of incidence. In the angular range of $\psi = 11-20^\circ$ for Si and $15-23^\circ$ for SiC, the sputtering occurs only from the first layer. It is seen that the threshold angle is a bit smaller in the case of Si than for SiC. As results for high initial energy show that, in general the sputtering yield is large in the case of SiC. These dependences allow choosing an angle of incidence for an effective sputtering at given initial energy.

In Figure 5a,b the sputtering yields of Si(001) and SiC(001) surfaces subdivided into sputtering by the first three surface layers versus the energy of incident Ne$^+$ ions are shown at $\psi = 10^\circ$. It should be noted that the elastic energy losses of the scattered particles are considerably smaller than the inelastic ones in a region of glancing scattering [9].

![Figure 5. Sputtering yield of Si(001) (a) and SiC(001) (b) versus energy of incident Ne$^+$ ions at $\psi = 10^\circ$](image)

The threshold energy of sputtering is about 1 keV for these cases. There is more drastic increase of sputtering yield in the beginning of dependences for Si than for SiC. It is seen that the main contribution to the total sputtering comes from the sputtering of the first layer. Moreover, in the energy range of 0.5-1.5 keV for Si and 1-3 keV for SiC, the sputtering occurs only from the first layer. Further increasing of the ion energy results in increasing the contribution from second and third layers.

The contribution to sputtering from the third layer is larger than the one from the second layer as the atomic rows in the second layer lies directly under the one of the first layer in the $<110>$ direction. Two local maxima at 2.5 and 4 keV are observed in the total sputtering yield dependence in the case of Si. Sputtering from the first layer gives a basic contribution to the first maximum while the second maximum is formed by atoms ejected from the second and third layers. In the case of SiC the maximum of total dependence is formed by atoms ejected from the second layer. These results show that by choosing an angle and an energy of incidence one can produce layer-by-layer sputtering of Si(001) and SiC(001) surfaces. For the realization of the layer-by-layer sputtering mechanism it is nessesary that a part of the ion energy, corresponding to the normal components of its velocity, will be lower than a threshold of sputtering of atoms of a layer, next to the surface one, i.e. $E_i \sin^2 \psi_i < E_d$, where $E_i$ is the ion energy before the $i$th collision, $\psi_i$ is the angle between the ion movement direction and the semichannel axis before the $i$th collision, $E_d$ – the energy of displacement of atoms of a second layer (in the case considered the bottom chain of semichannel).
In Figure 6 the azimuthal angular dependences of the sputtering yield are compared for Si(001) and SiC(001) surfaces at 5 keV Ne$^+$ ion bombardment, $\psi =10^\circ$. Main maxima and minima of dependences are observed in low crystallographic directions and near them. They are caused by the existence of original semichannels and channels in these directions. Thus, there is a good correlation between the sputtering yield dependences and crystallographic structures of studied crystals.

![Figure 6](image)

**Figure 6.** Sputtering yield of Si(001) and SiC(001) versus azimuth angle of incidence at $E_0 =5$ keV, $\psi =10^\circ$.

From the comparison of the two curves it is seen that at some values of azimuth angle, instead of the peaks of sputtering yield of Si(001) the minima of sputtering yield of SiC(001) are observed. This difference is caused by differences of binding energies, lattice parameters and, of course, compositions of these single crystals. In most range of the azimuth angle of incidence the sputtering yield for SiC is larger than the one for Si.

**Conclusion**

It was shown that in case of Be$^+$ and Se$^+$ ions implantation into GaAs(001) the main peak of the implanted depth distributions is considerable shallow, the range for Se is shallower and the half-width of profile for Se$^+$ is narrower than that for Be$^-$ ions. The obtained results allow to selecting the optimum for implanted depth distributions with demanded shape in narrow near-surface area (5-10 atomic layers) of crystals production.

At sufficiently small grazing angles ($\psi < 9^0$) the sputtering processes do not take place due to impossibility of ion penetration through surface in the case of perfect surface. In the angular range $9^0 \leq \psi \leq 15^0$ the monotonous increasing of the total sputtering yield is observed. The peculiarities of formation of PKR atoms at grazing ion incidence beam on an atomically smooth surface of a single crystal promotes its layer-by-layer sputtering. In these conditions it is possible to achieve successive removal of layers without disturbance of the next layer at removal of the previous one. Ion bombardment at grazing angles reduces considerably the influence of effect of crater walls and ion mixing on results of layer-by-layer analysis and increase its accuracy and sensitivity.
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