Enhanced sputter yields of ion irradiated Au nano particles: energy and size dependence

Henry Holland-Moritz¹, Sebastian Scheeler²,³, Christoph Stanglmaier²,³, Claudia Pacholski²,³ and Carsten Ronning¹

¹ Institute for Solid State Physics, Friedrich Schiller University Jena, Max-Wien-Platz 1, D-07743 Jena, Germany
² Department of New Materials and Biosystems, Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, D-70569 Stuttgart, Germany
³ Institute for Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany

E-mail: henry.holland-moritz@uni-jena.de

Received 30 April 2015, revised 19 June 2015
Accepted for publication 24 June 2015
Published 23 July 2015

Abstract

Hexagonally arranged Au nanoparticles exhibiting a broad Gaussian-shaped size distribution ranging from 30 nm to 80 nm were deposited on Si substrates and irradiated with Ar⁺ and Ga⁺ ions with various energies from 20 to 350 keV and 1 to 30 keV, respectively. The size and energy dependence of the sputter yield were measured using high-resolution scanning electron microscopy image analysis. These results were compared to simulation results obtained by iradina, a Monte Carlo code, which takes the specifics of the nano geometry into account. The experimental sputter yields are significantly higher than simulated sputter yields for both bulk and the nano geometry. The difference can be clearly attributed to thermally driven effects, which significantly increase the measured sputter yields.

Keywords: sputtering, nanofabrication, nanoparticles, ion beams, ion solid interaction

(Some figures may appear in colour only in the online journal)

1. Introduction

Miniaturization is a buzzword in the development of new technologies. Nanoscience and nanotechnology are key disciplines for making devices and their elements smaller and more efficient. Nanoparticles (NPs) have already been introduced into everyday life [1–3]. However, some work still needs to be done to really make use of the mesoscopic properties of nanostructures. These properties are mainly dominated by surface effects like surface reconstruction, depletion, Fermi level pinning and band bending. Thus, the surface plays an important role due to the increased surface-to-volume ratio of nano structures compared to bulk counterparts.

There are many ways to fabricate and grow nanostructures, for example physical vapor (PVD) or chemical vapor deposition (CVD) [4, 5]. Such techniques work at or close to the thermal equilibrium, limiting e.g. solubility of doping atoms or various other desired defects in the lattice. Ion implantation is a widely used technique to tune the properties of materials [6–10] and overcome the restrictions of the thermal equilibrium. An important effect, when it comes to ion irradiation, is sputtering. Sputtering is well understood theoretically by Sigmund’s theory [11], as well as experimentally for bulk structures [12–15]. In nanostructures, sputtering is enhanced due to the higher surface-to-volume ratio [16]. This enhancement plays a major role, i.e. when it comes to the doping of nanostructures and the calculation of the doping concentration [17].

This work shows an approach of measuring the sputter yield of Au NPs, which are wet-chemically synthesized and subsequently deposited on a Si substrate by self-organization. We used high-resolution SEM imaging to determine the sputter yields for Ar⁺ and Ga⁺ ions of various energies. Also, the size dependence of the sputter yield was investigated. These results are compared to the MC code iradina [18], which takes into account the nanostructures’ geometry.
2. Methods and experiment

Gold nanoparticles were wet-chemically synthesized in toluene [19] using seeding growth approaches. The resulting Au NPs were covered with a polystyrene shell by ligand exchange and subsequently spin-coated onto clean silicon substrates according to [19, 20]. In figure 1(a), a representative scanning electron microscopy (SEM) image of a prepared Au NP array and the size distribution of the Au nanoparticles determined by transmission electron microscopy (TEM) image analysis are displayed.

These samples were subsequently irradiated with Ar⁺ or Ga⁺ ions. The Ar⁺ irradiations were performed using a general purpose ion implanter (High Voltage Engineering Europa). A FEI Helios i600 Nano Lab focused ion beam system (FIB) was used for the irradiations with Ga⁺ ions. In order to determine the energy dependence of the sputter yield, the samples were irradiated by Ar⁺ ions with various energies ranging from 20 to 350 keV; the Ga⁺ ion energy ranged from 1 to 30 keV. The total ion fluence for each sample was set to $3 \times 10^{15} \text{cm}^{-2}$ and the ion beam current was kept constant at 0.5 $\mu$A and 0.1 $\mu$A for Ar⁺ and Ga⁺ ions, respectively. In order to evaluate the diameter dependence of the sputter yield, the ion energy was kept constant at 95 keV for Ar⁺ and at 25 keV for Ga⁺ irradiations respectively. For the diameter-dependent investigation, the ion fluences for the Ar⁺ and Ga⁺ irradiations were chosen to be $2 \times 10^{15} \text{cm}^{-2}$ and $3 \times 10^{15} \text{cm}^{-2}$, respectively. With all these ion energies and fluences the size changes were significantly larger than the SEM resolution of about 1 nm. High-resolution scanning electron microscopy (SEM) images of the samples were taken before and after each irradiation step. The NP position on the sample for image recording was chosen randomly for the energy-dependent measurements. For the diameter dependence, the samples were marked/grooved with the Ga⁺ beam of the FIB system in order to find the same NP positions after the irradiation. As a rough approximation, the NPs were assumed to be spherical.

Up to 3500 NPs were evaluated per sample and ion energy. The cross sectional area of the NPs were determined by ImageJ [21]. An ellipse was automatically fitted to the NPs, if they showed a certain threshold circularity of 0.3. If a NP did not show at least this circularity, it was not evaluated in the further process. The areas covered by the ellipse before and after the irradiation were used to calculate the sputter yield according to

$$Y = \frac{\rho_{\text{at}} \cdot \Delta V}{\Phi \cdot A_0} = \frac{4\rho_{\text{at}}}{3\sqrt{\pi} \Phi \cdot A_0} \cdot \left(A_{0}^{3/2} - A_{i}^{3/2}\right),$$

where $Y$ is the sputter yield, $\rho_{\text{at}}$ is the target materials atomic density, $\Delta V$ the volume change due to the irradiation, $\Phi$ the ion fluence, and $A_0$ and $A_i$ the average cross section of the NPs before and after the irradiation, respectively. For the ion energy-dependent experiments, the mean value of the NP areas were used for calculation, while for the diameter dependence the areas of exactly the same NPs were taken into account.

Monte Carlo (MC) simulations were performed with the code iradina [18] in order to calculate the sputter yields and predict the decrease in volume of the NPs. This code is based on corteo [22] and takes into account the nanoscale geometry. The binary collision approximation (BCA) is used and free-standing NPs are simulated. Also, the simulation takes place at virtually 0 K. Ten thousand ions were considered for each simulation. The material parameters for Au were: a displacement energy of 25 eV, a lattice binding energy of 2 eV and a surface binding energy of 3 eV [23]. The structure’s surface of the NP was described analytically by a sphere. The simulation for the nano geometry was performed for a free-standing spherical Au NP with a diameter of 50 nm irradiated with Ar⁺ ions of various energies. For diameter-dependent simulations, the ion energy was set constant at 95 keV and 25 keV for Ar⁺ and Ga⁺, respectively, and the particle diameter was varied. The bulk geometry was described by an Au cuboid with periodic boundary conditions in the directions.

Figure 1. (a) Representative SEM image of a gold NP array fabricated by spin-coating of polystyrene-coated gold NPs onto silicon substrates. Scale bar: 200 nm. (b) Size distribution determined by TEM of wet-chemically synthesized Au nanoparticles.
3. Results and discussion

3.1. Energy dependence

Figure 2(a) shows the determined sputter yields for the Ar⁺ irradiation of Au particles with an average diameter of 50 nm as a function of ion energy. The red data points represent the experimental results, while the blue and green dots denote the MC simulation results by iradina for nano and bulk geometries. The calculated sputter yield shows a steep increase with increasing energy for both geometries (bulk and NPs). The bulk sputter yield reaches its maximum of about 4 atoms/ion at an ion energy around 20 keV and then decreases with increasing energy, which is the typical energy dependence observed for flat surfaces and in agreement with references [24, 25]. The MC simulation for the NPs shows an increase of the sputter yield up to 15 atoms/ion at an ion energy of 100 keV. At this ion energy, the ion range is comparable to the NP size of around 50 nm. The MC simulation shows a considerably higher sputter yield for the spherical nanostructure than for bulk geometry. The reason for the increased sputtering on nanostructures is their increased surface to volume ratio. Figure 2(c) illustrates this situation: the collision cascade extends mainly inside the target for the bulk situation, and only a few recoils move towards the surface and have enough energy to overcome the surface binding energy to leave the target. A similar ion trajectory is also shown for an ion hitting a nanostructure with spherical cross section. Here, the damage cascade fills almost the whole NP. The cascade has more intersection points with the structure’s surface, which leads to an increased number of sputtered atoms.

The experimental values, which are shown as red squares in figure 2(a), follow the trend given by the MC simulations of the nano geometry for small ion energies up to 100 keV. However, there is a notable shift of the maximum value of experimental sputter yield, which is at about 50 keV instead of 100 keV. The sputter yield for the experimental results in this regime is also higher than the simulated sputter yield by about 5 atoms/ion. For ion energies in the regime above 100 keV, the experimental values show a large spread. The value at 110 keV is the smallest value measured by the experiment; for energies larger than 250 keV, the spread of the data points decreases and the experimentally obtained values approach the simulation results for higher ion energies. In any case, the experimental results are larger than the simulated iradina bulk values. The discrepancy of simulation and experiment arises from several reasons, which will be explicitly addressed in the following. First, one can consider that the basic assumptions of the MC code are not accurate. In our simulation, a single, freestanding NP is represented, which neglects ion–substrate interactions as well as interactions between NP and substrate, for example burying of particles as shown in [26]. Additionally, iradina uses the binary collision approximation, which allows only the ejection of single atoms. However, the majority of sputtered atoms is ejected as clusters composed of up to thousands of atoms, as suggested by molecular dynamic (MD) simulations for a similar situation with a high atomic mass target [16]. Furthermore, the MC code iradina calculates all processes at 0 K, which is obviously not true for the experiment. The ion beam introduces thermal energy to the NPs, which leads to a considerable amount of thermally evaporated atoms, as discussed in detail in reference [16].

The decreasing of the sputter yields above 100 keV, which follows no clear trend, can be understood when taking a closer look at a representative SEM image of an irradiated sample shown in figure 3(a) and the analysis method. The image shows a sample irradiated with 100 keV Ar⁺ ions. First, one can see many small dots around the gold NPs, which are Au atoms/clusters sputtered in a forward direction from the NPs. They are redeposited at the substrate surface. Secondly, it is noticeable that different NPs reacted quite differently to the ion bombardment even though they were almost identical prior to irradiation (compare figure 1). Some NPs, such as the one marked with #1, did not change their shape at all, while other NPs, such as NP #2, completely vanished. Many other
NPs, such as NP #3, changed their shape dramatically and seem to sink into the Si substrate. A possible explanation for the latter two effects is the large amount of thermal energy transferred to the NPs by the ion beam. The NPs have a small volume, a high surface-to-volume ratio and have a low thermal contact/conductivity to the Si substrate. The introduced ion energy is finally converted into thermal energy, which cannot dissipate quickly. Another ion may impinge while the temperature is still high, heating the NP even more. Let us assume that one ion transfers its 100 keV of energy to an Au NP as thermal energy. With a diameter of 30 nm the NP contains about 8.4 × 10^5 atoms. This leaves about 0.1 eV/atom and, according to \( E = k_B \cdot T \), would result in a temperature increase of about 1000 °C; if thermal losses such as radiation, heat conduction and evaporation of atoms are neglected. Note, this simple estimation does not account for the extreme non-equilibrium process of ion irradiation. As observed in several MD simulations [16, 27–30], material is molten locally due to ion impacts. Zimmermann and Urbassek [30] show with MD simulations that a 9 nm particle is heated completely up to 1000 °C by a single ion impact. Since the molten material and with it most energetic atoms of the NP are expelled in clusters [16, 30], most thermal loss is due to the ejection of this material. With the same incident ion energy, small NPs are affected more by such thermal effects than by larger ones with the same incident ion energy. Further evidence for the thermally driven evaporation of material can be seen at NP #3 in figure 3(a). This NP shows so-called fingers, bridges and slingshots, which arise due to the ejection of heated and molten material. For the irradiation of bulk targets, similar effects have been shown by Nordlund et al [27] in MD simulations. All these thermal effects, which are evident from the SEM in figure 3(a), are not considered in MC codes at all.

The pronounced effect on small NPs can be seen in figure 3(b). Here, the size distributions of NPs are shown before and after the Ar^+ irradiation with 100 keV (left-hand side) and 110 keV (right-hand side). One can clearly see that the Gaussian shape is conserved in both cases. The mean value of the distribution shifts slightly towards smaller NPs for both ion energies, of course, due to sputtering. However, when we compare smaller NPs, we observe that the number of NPs smaller than 40 nm is higher after irradiation with 100 keV ions than with 110 keV ions. There are two reasons for this: on one hand, some small NPs simply vanish and are not counted by the software. On the other hand, some of these NPs were not taken into account by the image analysis software (see above), as they were too deformed. This leads to an apparent increase of the mean diameter for the NPs after the irradiation, which resulted in the calculation of a smaller sputter yield for the 110 keV experiment. For the ion energies below 110 keV and energies larger than 200 keV, more of the smaller NPs survive, which leads again to a more realistic sputter yield. The higher survival rate can be explained by the higher ion range in the material. High-energy ions penetrate through the NPs, depositing less energy in total than a lower energy ion which remains in the NP. For example, at 250 keV, an Ar^+ ion has an average projected range of 74 nm in Au, according to TRIM (Transport of Ions in Matter) [31]. At this energy, most of the NPs with a diameter of 50 nm or less can be expected to be traversed by the ions.

When high-energy ions penetrate through the complete NP, ion beam mixing starts at the NP–substrate interface. Due to the elevated temperatures, Au silicate is formed [32, 33], which leads to preferential sputtering of silicon from this alloy. This reduces the sputter yield of gold and can be considered as a reason for the lower sputter yields at higher energies. The formation of such an alloy can be seen at NP #2 in figure 3(a). At the position where the Au NP once was the substrate appears brighter than the surrounding area due to the mass contrast in SEM imaging. Most likely this is gold silicate, which remains in the substrate. The NP on top is sputtered away and mixed into the substrate.

Another possible explanation for the large spread of the experimentally obtained sputter yields is given by the fact that for all ion energies the same ion beam current was used. Different heating rates due to the different input powers (ion energy × ion flux) of the material for different energies are expected. Therefore, smaller NPs are affected in a different manner in different energy regimes, which causes a systematic variation of the results.
In figure 2(b) the experimental sputter yields of Au NPs are shown after ion irradiation with low energetic Ga\(^+\) ions together with respective MC simulations as a function of the ion energy. Again, these data points show the experimental results determined by mean values of the NP diameters. Up to an ion energy of 12 keV, the measured sputter yields are comparable to the MC simulations, except the value at an ion energy of 10 keV. With increasing ion energy, the experimentally obtained sputter yield values show a steep increase. At the ion energy of 30 keV the experimental value is about 3 times higher than the value obtained by iradina. In these experiments, the data points do not show as large a spread as with the higher energy Ar\(^+\) irradiation. Most of the effects described above, which may result in a large particle-to-particle variation, are not applicable in these experiments, because the ion energies were quite low compared to the Ar\(^+\) irradiations and the ion beam current was much lower, at 0.1 \(\mu\)A. This leads to lower input powers over the whole energy range and thermally driven effects are less pronounced. Furthermore, the ion range of Ga\(^+\) is low for the investigated energies. The maximum ion range in Au is 7.7 nm for 30 keV Ga\(^+\) ions, according to SRIM [34]. Nevertheless, it was also noticed that very small NPs vanished, albeit the effect was less pronounced, occurring only for fewer and smaller NPs.

Overall, the higher experimental sputter yield values compared to the simulation results can be explained by the fact that the MC code neglects thermal effects such as energy deposition as heat. Also, heat spike effects which lead to collective cluster sputtering are not considered in the simulation.

### 3.2. Size dependence

In figure 2(b) the experimental sputter yields of Au NPs are shown after ion irradiation with low energetic Ga\(^+\) ions together with respective MC simulations as a function of the ion energy. Again, these data points show the experimental results determined by mean values of the NP diameters. Up to an ion energy of 12 keV, the measured sputter yields are comparable to the MC simulations, except the value at an ion energy of 10 keV. With increasing ion energy, the experimentally obtained sputter yield values show a steep increase. At the ion energy of 30 keV the experimental value is about 3 times higher than the value obtained by iradina. In these experiments, the data points do not show as large a spread as with the higher energy Ar\(^+\) irradiation. Most of the effects described above, which may result in a large particle-to-particle variation, are not applicable in these experiments, because the ion energies were quite low compared to the Ar\(^+\) irradiations and the ion beam current was much lower, at 0.1 \(\mu\)A. This leads to lower input powers over the whole energy range and thermally driven effects are less pronounced. Furthermore, the ion range of Ga\(^+\) is low for the investigated energies. The maximum ion range in Au is 7.7 nm for 30 keV Ga\(^+\) ions, according to SRIM [34]. Nevertheless, it was also noticed that very small NPs vanished, albeit the effect was less pronounced, occurring only for fewer and smaller NPs.

Overall, the higher experimental sputter yield values compared to the simulation results can be explained by the fact that the MC code neglects thermal effects such as energy deposition as heat. Also, heat spike effects which lead to collective cluster sputtering are not considered in the simulation.

In figure 4(a), the sputter yields for both the simulation and experiments are shown for 95 keV Ar\(^+\) irradiated Au NPs as a function of the size of the Au NPs. According to the iradina simulations, the sputter yield increases with increasing diameter until it reaches a maximum, where the NP size is comparable to the ion range at this specific ion energy. In this increasing regime, the sputtering is mostly forward sputtering [35], since the ion range is large compared to the NP size and the ions interact mainly with the substrate. At the maximum, the damage cascade propagates over almost the whole NP and has the largest intersection area with the surface of the NP. The sputter yield decreases again for increasing diameters; the main fraction of the sputtering is due to side and backward sputtering [35]. The light red cross-shaped data points show the experimental sputter yields for single NPs. Again there is a large spread of the data points. For example, NPs with a diameter around 39 nm show sputter yields between 1 and 30 atoms/ion. The spread of data points observed for the energy-dependent experiments with Ar\(^+\) ions was explained by the large deformation of the NPs by ion bombardment and the way the image analysis worked. The deformation effects have not been observed in size-dependent experiments, so the reason for the large spread must be different. One reasonable explanation is channeling. As discussed by Greaves et al [16], the sputter yield strongly depends on the orientation of the NPs’ lattice towards the ion beam. If the ion arrives in channeling direction, it passes a 20 nm Au NP without depositing much of its energy, but if the ion impacts in a random direction, the sputter yield is much higher [16]. Since the NPs are spin-coated onto the substrate, their orientation towards the ion beams is random. Some NPs are facing the beam ion in any preferential lattice direction and some in random direction. This might explain the difference between the maxima and the minima sputter yields for each NP size. Another effect is redeposition of sputtered material on surrounding NPs. Smaller NPs have a larger sputter yield, larger NPs a smaller one. Since larger NPs cover a larger solid angle, the probability to collect sputtered atoms from the surrounding NPs is larger. This might lead to a delayed sputtering for mid-range and larger NPs, a similar situation to Oswald ripening.

The variation of sputter yields for NPs with similar diameter was also observed in the experiments with Ga\(^+\) ions, as shown in figure 4(b). Here it is much less pronounced, as the
ion range is much smaller compared to the size of the NPs. Whereas, for the irradiation with 95 keV Ar⁺ ions the average NP size matches the ion range, the projected ion range for Ga⁺ ions with 25 keV energy is only 6.7 nm according to SRIM. Thus, the ion–solid interaction processes mainly occur in the upper hemisphere of the NPs with average and larger sizes. Therefore, the channeling and shrinking/deformation effects are less pronounced here.

The red data points in figure 4 show the average sputter yield values calculated from data points of NPs in intervals of 1 nm. For the Ar⁺ irradiation, the average values for small sizes up to 45 nm fit the simulated data very well, while for larger sizes the experimentally obtained sputter yield is increased up to a factor of 3 compared to the MC simulation. This behavior cannot be explained by the models provided. The sputter yields obtained for Ga⁺ irradiations also show for the mean values less variation and smaller statistical errors. The values of the experimental sputter yields are twice as large as the iradina results. When comparing the results for Ga⁺ irradiations to the model provided by Järvi et al [36, 37], they fit quite well to the extrapolation of the model for larger NP sizes. As shown by MD simulations, the major driving force in the sputtering process is cluster emission [16]. The trend of the experimental results for the Ga⁺ sputter yields proceeds parallel to the curve of the iradina results and decreases with larger NP diameter, as the presented model predicts. This suggests that there is a systematic variation in the experiments for Ar⁺ irradiated NPs, which shifts the results towards higher sputter yields for larger NPs and remains to be studied by future experiments.

With its higher density and mass, ion irradiated Au seems to show more pronounced thermally driven effects than, for example, semiconductors [17]. Because the damage cascade is dense in dense target materials, heat spikes arise from the collision cascade and lead to the ejection of molten material [16, 27]. This enhances the sputter yield and sets a limit for the application of MC simulations. There are more limitations of the used MC code. Another critical parameter in the input data is the surface binding energy (SBE). The SBE decreases especially for small particles and large curvatures and a small SBE would increase the sputter yield. However, even at an unrealistically small SBE of 0.1 eV, the simulated sputter yield for NPs is still smaller than the experimentally determined value of the sputter yield for the Ga⁺ irradiation shown in figure 4. The BCA, which is typical for most MC codes, is not accurate in the heat spike regime, since the cascade is not linear anymore [28, 38, 39]. Here, MD simulations deliver more realistic results [16, 27, 28, 40]. Also, other thermally driven effects like evaporation of heated material are not included in MC simulations. Finally, iradina is not a dynamic simulation, which means the parameters’ density and structure size remain constant. Since sputtering is strongly size dependent, a dynamic MC simulation could at least cover this effect. A new code dealing with this point is described by Möller [41].

4. Conclusions

An approach for the determination of the sputter yields of Au NPs was demonstrated. It is based on the automated analysis of a large number of high-resolution SEM images taken before and after ion irradiation. In parallel, simulations of sputtering were performed using the MC, BCA based simulation tool iradina.

For the ion energy–dependent measurements and a fixed Au average particle diameter of 50 nm, irradiations with Ar⁺ showed a higher sputter yield than the simulation results for below 100 keV. Thermally driven effects were clearly observed for higher ion energies, which led to higher experimental sputter yields. A strong deformation of NPs was observed for energies above 100 keV. This led to a strong fluctuation of the data points due to the low number of high-resolution SEM images analyzed. In any case, the sputter yields were higher than the calculated bulk sputter yield. The reason for the deviation between simulation and experiment is that the basic assumptions of the MC code with the BCA neglects thermally driven effects like heat spikes and cluster ejection. Extreme deformations of the NPs by the thermally driven effects were only observed in the experiments carried out with Ar⁺ ions in the energy regime between 100 keV and 200 keV. The experimentally determined sputter yields for Ga⁺ ions were higher than the simulated sputter yields for most energies, except for small ion energies. The slope of the increase of the energy dependence of the sputter yield is steeper than the simulation predicts, since the experimental sputter yield is in most cases larger than the simulated one and the difference is increasing with increasing ion energy. The measured sputter yields’ for a fixed ion energy showed a large variation for the yields of individual NPs of the same size. This may be due to the different lattice orientations of various NPs towards the ion beam, as channeling will lower the sputter yield for selected orientations. Another effect is the redeposition of sputtered material on surrounding NPs. The spread of sputter yields for individual NPs was larger in the irradiation with Ar⁺ ions than with Ga⁺ ions. In the case of Ar⁺ ions, the average sputter yields tended to increase with increasing NP diameter, while the experimental Ga⁺ yields were twice as large as the simulation results, but followed the same dependence on the NP diameter.

The presented results show that sputtering is an important issue when irradiating nanostructures with ion beams for doping, shaping or other modifications. Monte Carlo simulations such as iradina provide a good qualitative prediction of the number of sputtered atoms in nanostructures, but especially when irradiating heavy or dense materials, the sputter yield is underestimated.

Acknowledgments

We thank Patrick Hoffmann from the University of Jena for helping us in performing experiments at the accelerator and Andreas Johannes for his valuable comments to the
manuscript. We also thank the BMBF for funding (BMBF project PhoNa, contract no. 03IS2101E & 03IS2101A) and the Max Planck Society.

References

[1] Daniel M-C and Astruc D 2004 Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology Chem. Rev. 104 293–346

[2] Shipway A N, Katz E and Willner I 2000 Nanoparticle arrays on surfaces for electronic, optical, and sensor applications Chem. Phys. Chem. 1 18–52

[3] Pankhurst Q A, Connolly J, Jones S K and Dobson J 2003 Applications of magnetic nanoparticles in biomedicine J. Phys. Appl. Phys. 36 R167

[4] Mattox D M 2010 Handbook of Physical Vapor Deposition (PVD) Processing (Oxford: William Andrew)

[5] Dobkin D M and Zuraw M K 2003 Principles of Chemical Vapor Deposition (Dordrecht: Springer)

[6] Davi E A, Rizza G, Mink M P, Vredenberg A M and Habrank F H P M 2009 Ion beam shaping of Au nanoparticles in silica: particle size and concentration dependence J. Appl. Phys. 105 074305

[7] Ronning C et al 2010 Tailoring the properties of semiconductor nanowires using ion beams Phys. Status Solidi B 247 2329–37

[8] Cao Y, Li X and Gu M 2014 Super-resolution nanofabrication with metal-ion doped hybrid material through an optical dual-beam approach Appl. Phys. Lett. 105 263102

[9] Sharma P A et al 2014 Ion beam modification of topological insulator bismuth selenide Appl. Phys. Lett. 105 242106

[10] Takaoka G H, Hamaguchi T, Takeuchi M and Ryuto H 2014 Surface modification using ionic liquid ion beams Nucl. Instrum. Methods Phys. Res. B 341 32–6

[11] Sigmund P 1969 Theory of sputtering. I. Sputtering yield of amorphous and polycrystalline targets Phys. Rev. 184 383–416

[12] Andersen H H and Bay H L 1975 Heavy-ion sputtering yields of gold: further evidence of nonlinear effects J. Appl. Phys. 46 2416–22

[13] Blank P and Wittemaack K 1979 Energy and fluence dependence of the sputtering yield of silicon bombarded with argon and xenon J. Appl. Phys. 50 1519–28

[14] Oliva-Florio A, Baragiola R A, Jakas M M, Alonso E V and Ferrón J 1987 Noble-gas ion sputtering yield of gold and copper: dependence on the energy and angle of incidence of the projectiles Phys. Rev. B 35 2198–204

[15] Feder R, Bundesmann C, Neumann H and Kauschenbach B 2014 Ion beam sputtering of germanium—energy and angular distribution of sputtered and scattered particles Nucl. Instrum. Methods Phys. Res. B 334 88–95

[16] Greaves G, Hinks J A, Busby P, Mellors N J, Ilinnov A, Kuronen A, Nordlund K and Donnelly S E 2013 Enhanced sputtering yields from single-ion impacts on gold nanorods Phys. Rev. Lett. 111 065504

[17] Johannes E et al 2014 Enhanced sputtering and incorporation of Mn in implanted GaAs and ZnO nanowires J. Phys. Appl. Phys. 47 394003

[18] Borschel C and Ronning C 2011 Ion beam irradiation of nanostructures—a 3D Monte Carlo simulation code Nucl. Instrum. Methods Phys. Res. B 269 2133–8

[19] Stanglmair C, Scheele S P and Pacholski C 2014 Seeding growth approach to gold nanoparticles with diameters ranging from 10 to 80 nanometers in organic solvent Eur. J. Inorg. Chem. 2014 3633–7

[20] Ulrich S, Scheele S P, Pacholski C, Spatz J P and Kudera S 2013 Formation of large 2D arrays of shape-controlled colloidal nanoparticles at variable interparticle distances Part. Part. Syst. Char. 30 102–8

[21] Schneider C A, Rashband W S and Eliceiri K W 2012 NIH image to image: 25 years of image analysis Nat. Methods 9 671–5

[22] Schiettekatke F 2008 Fast Monte Carlo for ion beam analysis simulations Nucl. Instrum. Methods Phys. Res. B 266 1880–5

[23] Hofssäss H, Zhang K and Mutzeke A 2014 Simulation of ion beam sputtering with SDTrimSP, TRIDYN and SRIM Appl. Surf. Sci. 310 134–41

[24] Bierrose J P and Eckstein W 1984 Sputtering studies with the Monte Carlo program TRIM.SP Appl. Phys. A 34 73–94

[25] Eckstein W 2008 Sputtering yields Vacuum 82 930–4

[26] Klimmer A, Ziemann P, Biskupek J, Kaiser U and Flesch M 2009 Size-dependent effect of ion bombardment on Au nanoparticles on top of various substrates: thermodynamically dominated capillary forces versus sputtering Phys. Rev. B 79 153427

[27] Nordlund K, Taranu J, Keinonen J, Donnelly S E and Birtcher R C 2003 Atomic fingers, bridges and slingshots: formation of exotic surface structures during ion irradiation of heavy metals Nucl. Instrum. Methods Phys. Res. B 206 189–93

[28] Nordlund K, Ghaly M, Averback R S, Caturia M, Diaz de la Rubia T and Taranu J 1998 Defect production in collision cascades in elemental semiconductors and fcc metals Phys. Rev. B 57 7556–70

[29] Anders C, Bringa E M and Urbanek H M 2015 Sputtering of a metal nanofoam by Au ions Nucl. Instrum. Methods Phys. Res. B 342 234–9

[30] Zimmermann S and Urbanek H M 2008 Sputtering of nanoparticles: molecular dynamics studies of Au impact on 20 nm sized Au nanoparticles Int. J. Mass Spectrom. 272 91–7

[31] Ziegler J F, Ziegler M D and Biersack J P 2010 SRIM—the stopping and range of ions in matter Nucl. Instrum. Methods Phys. Res. B 268 1818–23

[32] Lau S S, Tsaur B Y, von Allmen M, Mayer J W, Strizcker B, White C W and Appleton B 1981 Ion-beam mixing of metal-semiconductor eutectic systems Nucl. Instrum. Methods 182–183 97–105

[33] Mayer J W, Tsaur B Y, Lau S S and Hung L S 1981 Ion-beam-induced reactions in metal-semiconductor and metal-metal thin film structures Nucl. Instrum. Methods 182–183 1–13

[34] Ziegler J F, Biersack J P and Ziegler M D 2008 SRIM: The Stopping and Range of Ions in Matter (Lulu.com)

[35] Nettiadi M L, Sandoval L, Urbaske H M and Möller W 2014 Sputtering of Si nanospheres Phys. Rev. B 90 045417

[36] Järvi T T, Pakarinen J A, Kuronen A and Nordlund K 2008 Enhanced sputtering from nanoparticles and thin films: size effects Europhys. Lett. 82 26002

[37] Järvi T T and Nordlund K 2012 Sputtering of freestanding metal nanocrystals Nucl. Instrum. Methods Phys. Res. B 272 66–9

[38] Sigmund P 1977 Sputtering processes: collision cascades and spikes Inelastic Ion–Surface Collisions ed N H Tolk, J C Tully, W Heiland and C W White (New York: Academic) pp 121–52

[39] Jakas M M and Bringa E M 2000 Thermal-spike theory of sputtering; the influence of elastic waves in a one-dimensional cylindrical spike Phys. Rev. B 62 824–30

[40] Krasheninnikov A V and Nordlund K 2010 Ion and electron irradiation-induced effects in nanostructured materials J. Appl. Phys. 107 071301

[41] Möller W 2014 TRIDYN—collisional computer simulation of the dynamic evolution of 3-dimensional nanostructures under ion irradiation Nucl. Instrum. Methods Phys. Res. B 322 23–33