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Published in:
Journal of Physics D: Applied Physics

DOI (link to publication from Publisher):
10.1088/0022-3727/42/20/205303

Publication date:
2009

Document Version
Publisher's PDF, also known as Version of record

Link to publication from Aalborg University

Citation for published version (APA):
Formation of surface nanostructures on rutile (TiO₂): comparative study of low-energy cluster ion and high-energy monoatomic ion impact

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Received 15 May 2009, in final form 31 August 2009
Published 24 September 2009
Online at stacks.iop.org/JPhysD/42/205303

Abstract
The formation of nanostructures on rutile (TiO₂) surfaces formed after the implantation of kiloelectronvolt-energy Ar⁺ₙ cluster ions and megaelectronvolt- to gigaelectronvolt-energy multiply charged heavy ions (I⁺ₙ, Ta⁺ₙ and U⁺ₙ) is studied. Despite the differences in stopping and energy transfer mechanisms between the kiloelectronvolt-energy cluster ions and megaelectronvolt-energy monoatomic ions, their impacts lead to a similar type of surface damage, namely craters. For the cluster ion implantation the craters are caused by the multiple-collision effect (dominated by nuclear stopping) and the high density of energy and momentum transferred to the target, while for the case of megaelectronvolt multiply charged ions the craters are probably formed due to the Coulomb explosion and fast energy transfer caused by the electronic stopping. At ion energies in the gigaelectronvolt range, nanosize protrusions, so-called hillocks, are observed on the surface. It is suggested that electronic stopping leads to the formation of continuous tracks and the transferred energy is high enough to melt the material along the whole projectile path. Elastic rebound of the tension between the molten and solid state phases leads to liquid flow, expansion and quenching of the melt, thus forming the hillocks. Atomic force microscopy measurements carried out under different environmental conditions (temperature and atmosphere) suggest that the damaged material at the nanosize impact spots has very different water affinity properties (higher hydrophilicity or water adsorption) compared with the non-irradiated rutile surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Ion beam technologies have attained an advanced stage of development. The interest in both research and industrial areas comes from the possibility of modifying physical and chemical properties of materials, even on the nanometre scale, either through the energy deposition by the ions and/or by the implanted ion species themselves. Energetic ions offer unique capabilities for structuring of material and for tailoring of functional properties. In particular, swift heavy ions are of considerable interest due to specific effects related to electronic stopping, formation of latent tracks and radiation defects that might be utilized for various applications [1–4].

At the same time, novel methods, such as cluster ion beams, are under consideration for material modification on
the nanoscale. Cluster ion implantation is rather different from that of monoatomic ion implantation because atomic clusters generate multiple-collision effects with overlapping radiation cascade zones causing severe radiation damage [4–6]. The effect of the high density of the energy transferred from the cluster at the beginning of energetic impact can be compared with a meteorite–planet collision and typically results in the formation of nanoscale damages such as craters [7, 8]. Even though cluster–solid interaction has been intensively studied for the last 10–15 years, the physics of these phenomena is still not very well understood and a consistent model for cluster stopping in matter does not exist.

In this work we compare nanostructures on rutile (TiO$_2$) surfaces formed after the impact of kiloelectronvolt-energy Ar$^{+}_n$ cluster ions and megaelectronvolt- to gigaelectronvolt-energy multiply charged I$^{+}_q$, U$^{+}_q$ and Ta$^{+}_q$ ions. The interest for TiO$_2$ comes from a wide range of technological applications of this versatile material [9], for instance, good biocompatibility [10] and important catalytic and photocatalytic properties [11–14]. From an ion impact point of view it is important to note that many physical and chemical properties of TiO$_2$ can be influenced by ion implantation.

2. Experimental section

Samples of TiO$_2$ (rutile (1 0 0)), obtained from MTI Corporation, were prepared as $\approx 1$ mm thick plates of few mm$^2$ area and implanted by cluster and monoatomic ions.

Cluster ion implantation was carried out using the CIDA and PUCLUS facilities [15, 16]. The samples were bombarded by Ar$^{+}_n$, cluster ions with energies of 6.9, 11.5 and 17.25 keV/cluster in ultra-high vacuum of $5 \times 10^{-9}$ Torr at normal incident angle and room temperature. The fluences were kept low (ca $10^7$ cm$^{-2}$) in order to avoid overlapping of the impact areas. Some of the implanted samples were treated in 20% aqueous solution of HF for 30 min in order to selectively dissolve the damaged material from the ion impact regions.

Another set of samples was implanted by I$^{+}_q$ and I$^{10+}_q$ ions with energies of 40 MeV and 46 MeV, respectively, at normal incident angle and room temperature. The ions were delivered from the Uppsala 5 MV tandem accelerator. The ion fluences applied were in the range of $10^8$ cm$^{-2}$ for I$^{+}_q$ ions and $10^9$ cm$^{-2}$ for I$^{10+}_q$ ions. The ion fluence was determined from the irradiation time and the beam current, which were measured using a Faraday cup with an aperture of 1.0 cm$^2$ located behind the sample holder. Homogeneous irradiation over an area of $10 \times 10$ cm$^2$ was achieved by means of an electrostatic raster scanner.

One more series of samples was irradiated by heavy swift U$^{+}_q$ and Ta$^{+}_q$ ions at the UNILAC (GSI, Darmstadt). The initial ion energy of 11.4 MeV/u was degraded by a foil of 50 $\mu$m aluminium mounted in front of the sample, thus reducing the energy to about 1.2 GeV and 1 GeV for the U and Ta beams, respectively. By electron stripping, the charge state of the projectiles was adjusted to the equilibrium one, estimated to be distributed around 46+ and 42+ for U and Ta, respectively, before impinging on the target surface. Assuming the resulting charge state distribution is Gaussian, one can estimate the standard deviation to be roughly 3 charge units [17, 18]. Homogeneous irradiation of the samples was obtained by applying a broad defocused beam. All irradiations were performed under normal beam incidence and at room temperature. The fluences were in the range $10^8$–$10^{10}$ cm$^{-2}$.

The surfaces of the implanted samples were studied by atomic force microscopy (AFM) operated in the tapping mode (Ntegra-Aura, NT-MDT) using ultra-sharp (with a curvature radius of 2 nm) Si cantilevers. The AFM images were obtained in ambient atmosphere (relative humidity of ca 30%) at room and at elevated temperature (100 °C) as well as in a dry nitrogen atmosphere at room temperature. For the elevated temperature and the nitrogen atmosphere measurements the samples were kept at least 1 h under these conditions prior to imaging.

High resolution scanning electron microscopy (HR-SEM) study was performed using a LEO 1550 microscope equipped with a field emission gun (FEG). The FEG, together with the in-lens detector, allows one to apply very low electron beam currents, thus, reducing the charging effects of the samples.

Rutherford back-scattering (RBS) measurements were carried out at a Tandetron accelerator (Nuclear Physics Institute, Rež) using 1.7 MeV $^4$He$^+$ ions and a laboratory scattering angle of 170°. The spectra were obtained for random and channelling orientations of the beam with respect to the samples.

3. Results and discussion

3.1. Cluster ion implantation

AFM measurements carried out in ambient atmosphere on the cluster-implanted samples show the formation of small bumps (or hillocks) with a height of a few Å and a diameter of 10–20 nm (figure 1(b)). Since, no such bumps were observed on pristine rutile (figure 1(a)) and the spatial density of these defects corresponds to the implantation fluence, one can conclude that these nanostructures were produced by the cluster impacts. At the centre of some bumps small openings can be resolved revealing crater-like structures (see the inset in figure 1(b)). Rim-to-rim diameters of these craters are found to be 5–10 nm. These dimensions are very close to the lateral resolution limit due to the tip convolution effect of the used cantilevers. It is therefore not surprising that only some impact areas can be resolved as craters while others are imaged as hillocks. The resolution can be significantly improved by performing the AFM measurements in dry nitrogen atmosphere, which eliminates a thin liquid adsorbate layer that is always present on surfaces in ambient (humid) atmosphere. AFM images obtained in nitrogen atmosphere clearly show that each impact spot is a crater (figure 1(c)). This observation also suggests that the cluster impact sites are much more hydrophilic compared with pristine rutile, which is known as a hydrophobic material. This effect is similar to that found on TiO$_2$ under the UV irradiation [11] with the difference that the water affinity is not changed over the whole surface but is localized at the nanometre-size impact spots. Due to the radiation damage the crater areas contain numerous dangling bonds which can favour accumulation of water molecules.
Figure 1. AFM images of (a) pristine rutile and the samples implanted by Ar$^{+23}$ cluster ions with energies of (b) 11.5 and (c) 17.25 keV/cluster. The images (a) and (b) are obtained in ambient atmosphere while image (c) is recorded in dry nitrogen. Inset to (b) (top left corner) shows a magnified image of a crater with diameter of ca 12 nm. (Colour online.)

or hydroxyl groups that leads to the appearance of artificial centrally located protrusions in craters or complete conversion of craters into hillocks in the AFM images. In the dry nitrogen atmosphere the water effect is eliminated, thus resulting in a true crater structure.

Crater formation resulting from kiloelectronvolt-energy cluster–surface impacts has been predicted by numerous molecular dynamics simulations, for instance [19–21], and has experimentally been observed for different cluster species and types of substrate material [7, 8, 22, 23]. Crater formation can be explained by the multiple-collision effect leading to high density of energy and high momentum transferred from cluster to target atoms that initiates local compression and development of shock wave. The impact region becomes strongly disordered and the involved atoms possess high kinetic energy. A large fraction of them—mainly those close to the edges of the crater—obtain momenta directed away from the surface. This phenomenon leads to the outer rim formation which can be seen in figure 1.

Within the studied energy interval of 6.9–17.25 keV/cluster, the craters show no significant difference in diameter. The increase in energy should lead to higher projected ranges $R_p$ of the cluster constituents and deeper radiation damage. To estimate the depth of the radiation damage the samples were chemically etched that led to the formation of pits at the impact spots. However, for the above-mentioned interval of energies the depth difference of the etched pits is found to be very small from sample to sample; it is almost within the statistical error of the AFM measurements. These measurements therefore give only a rough estimation but not a quantitative dependence of the radiation damage depth on the cluster energy. To get such dependence, one would need to test a much wider interval of implantation energies which is unfortunately not achievable with our equipment. Nevertheless, the data on etching indicate the presence of the so-called ‘clearing-the-way’ effect, where the ‘front’ atoms of the cluster push target atoms out of the way of the ‘rest’ atoms leading to an increase in their $R_p$ [3, 24].

For instance, the measured mean depth of the etched pits for the 11.5 keV/cluster (500 eV/atom) sample is found to be 3.0 ± 1.0 nm, whereas SRIM-2003 [25] simulations yield an $R_p$ of 1.4 ± 0.6 nm for 500 eV Ar monomers in TiO$_2$. The simulated data are at least two times lower compared with the experimentally measured depth of the pits, thus demonstrating higher implantation depth for the cluster constituents.

3.2. Monomer ion implantation

Typical AFM images obtained for the iodine-implanted samples in ambient atmosphere are presented in figure 2. Whereas the complex (with a hillock inside) craters are observed on the sample implanted by 40 MeV I$^{9+}$ ions, only hillocks are found on the sample implanted by 46 MeV I$^{10+}$ ions. Changing the measurement conditions to dry nitrogen atmosphere leads to the disappearance of hillocks; only the simple craters are imaged. The reason for this phenomenon should be the same as for the samples implanted by clusters, i.e. change of water affinity at the ion impact spots. An additional proof for this is provided by the measurement of one of the samples also under heating up to 100 °C in ambient atmosphere. This heating should remove liquid adsorbate layer similar to the case of dry nitrogen environment. Indeed, one can see in figures 3(a) and (b) similar craters both for the sample measured in nitrogen and the heated one. Due to the rather high fluence for the sample implanted by the 46 MeV I$^{10+}$ ions some of the craters (damage areas) overlap and it is difficult to estimate crater parameters. However, it is easy to do for the sample implanted by a lower fluence of 40 MeV I$^{8+}$ ions. The crater diameters are found to be between 10 and 20 nm, which is slightly larger compared with the cluster case.
The observed surface damage is rather different for samples implanted by gigaelectronvolt uranium and tantalum ions (see figure 4(a)). In both cases, no craters but exclusively nanosize hillocks are found independent of the measurement conditions. The only difference is that the imaging resolution is better in dry nitrogen compared with ambient atmosphere. The hillock diameters measured at half height vary between 25 and 40 nm for both samples. However, the data scattering for hillock heights is much wider for the U-implanted sample, 1–5 nm, compared with the Ta-implanted one, 0.8–1.2 nm. Most of the hillocks show shapes very close to cylindrical ones (figure 4(b)). The AFM observations are supported by SEM ones. One of the images is presented in figure 5. It shows bright spots, which are round in shape, representing the cylindrical hillocks. Some of them contain small centrally located depressions at the top. Hillock diameters are measured to be $13 \pm 2$ nm. These values are lower compared with those obtained by AFM that is related to the well-known tip convolution effect which increases the lateral dimensions of nanometre-scale features. There were no such hillocks found by SEM on the megaelectronvolt irradiated samples.

To better understand the physics behind the crater and hillock formation found after the respective implantation by mega- and gigaelectronvolt multiply charged ions one should compare the energy transfer processes from the projectiles to the substrate as well as consider the phenomena related to the high charge state of the ions.

The hillock formation under the implantation of swift heavy ions has previously been observed on a number of various materials, see for instance [1, 4, 26, 27]. The formation of nanosize protrusions can be explained in terms of the thermal spike model, in which the energy transferred through the electronic stopping from the ion to the target leads to the melting of the material along the ion trajectory (latent track). The molten phase is pushed out and quenched forming the hillock. The electronic stopping power $S_e$ is one of the critical parameters because the radius of the latent track is known to increase with $S_e$ and at a certain value of radius ($\geq 3$ nm), the damage in the track becomes homogeneous. At
AFM image and (b) cross-sectional profile of one of the hillocks of sample implanted by 1.0 GeV Ta\textsuperscript{4+} ions measured in dry nitrogen atmosphere. (Colour online.)

Figure 4. (a) AFM image and (b) cross-sectional profile of one of the hillocks of sample implanted by 1.0 GeV Ta\textsuperscript{4+} ions measured in dry nitrogen atmosphere. (Colour online.)

Figure 5. SEM image of sample implanted by 1.2 GeV U\textsuperscript{4+} ions.

The thermal spike model the threshold is related to the condition that the energy is enough to surpass the melting temperature ($T > 2130$ K) in tracks on the time scale of $10^{-13}$–$10^{-11}$ s. The model agreed with the experimental data presented in the same paper for few different ion species as well as with the results presented elsewhere for 93 MeV Xe\textsuperscript{23+} implantation into TiO\textsubscript{2} and SrTiO\textsubscript{3} [29]. According to the SRIM-2003 code [25], the $S_e$ values are 13 keV nm\textsuperscript{−1} and 14 keV nm\textsuperscript{−1} for 40 MeV and 46 MeV iodine ions, respectively, used in our case. Thus, these values are lower than the calculated threshold and the energy transferred from the ion to the target is probably not enough to cause the formation of continuous amorphous ion tracks. For discontinuous tracks, the flow of molten material towards the surface is hindered and the formation of hillocks is obviously suppressed. In contrast, the $S_e$ values for the case of gigaelectronvolt Ta and U ions are 33.3 keV nm\textsuperscript{−1} and 46.8 keV nm\textsuperscript{−1}, respectively, i.e. far above the threshold for the continuous track formation with the molten phase along the whole track. Channelling RBS spectra (figure 6) show a higher yield of the back-scattered particles for the U-irradiated sample compared with the I-implanted one, supporting our suggestion about more pronounced damage introduced by the gigaelectronvolt ions.

Although the interaction of megaelectronvolt multiply charged iodine ions is dominated by electronic stopping, the formed tracks are most probably discontinuous. On the other hand, the high charge of the ions may induce a Coulomb explosion at the surface. It was recently shown by the molecular dynamics simulations that the Xe\textsuperscript{q+} ion implantation in Si led to the crater formation caused by Coulomb explosion [30]. The same scenario was suggested for the crater formation in the case of kiloelectronvolt-energy bombardment of TiO\textsubscript{2} surfaces by K\textsuperscript{q+} ions [31]. In our case, the situation is less clear because both the Coulomb explosion effect and the energy transfer due to the electronic stopping at the very beginning of the track should be considered. This energy transfer is to some extent similar to the high density of energy deposition on cluster impact that, as shown above, leads to the crater formation.
Hillock formation for the case of gigaelectronvolt-energy Ar+ implantations can most probably be ascribed to liquid flow given by elastic rebound of the tensions between the molten and solid state phases followed by expansion and quenching effects. Our experimental data and suggested explanation are consistent with earlier results and models of the hillock formation on TiO₂ surfaces covered with a thin (5 nm) layer of Pt and implanted by 1.2 GeV Ta ions [32]. The reason why in our case the hillocks are higher on impact of uranium ions compared with tantalum ones is probably the higher value of Sₑ for the case of U ions. It was shown elsewhere [33] for the case of swift heavy ion implantation of CaF₂ that hillock height is an increasing function of Sₑ.

4. Conclusions

In this study we compared the formation of radiation-induced hillocks on TiO₂ surfaces covered with a thin (5 nm) layer of Pt and implanted by 1.2 GeV Ta ions [32]. The reason why in our case the hillocks are higher on impact of uranium ions compared with tantalum ones is probably the higher value of Sₑ for the case of U ions. It was shown elsewhere [33] for the case of swift heavy ion implantation of CaF₂ that hillock height is an increasing function of Sₑ.

Acknowledgments

One of the authors (AM) acknowledges support from the Ministry of Education, Youth and Sport of the Czech Republic (project LC06041) and from CFS (project 106/09/0125).

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