Nanostructuring surfaces with slow multiply-charged ions

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***Abstract*- With the shrinking of semiconductor devices surface features and structuring become increasingly important. Generally, fast ions are used for modification of surfaces via ion beam writing. Their kinetic energy is not only dissipated close to the surface but also in deeper layers of the material. Associated radiation damage could become a problem in the production of novel 3D micro- and nanoelectromechanical systems (MEMS and NEMS). Slow (<1keV) multiply-charged ions as opposed to fast ions are a new tool for gentler structuring of surfaces at the nanometer-scale. The substrate is modified only at and slightly below the surface, opening the possibility of controlling electronic properties at the nanometer scale, vertically and horizontally. Materials under investigation are highly orientated pyrolytic graphite, single crystal insulators (quartz, mica, aluminum oxide), hydrogen-terminated single-crystal silicon, AsSe- and Se-glass and mylar foils. The materials modified by the ion irradiation are investigated with scanning probe microscopy (AFM, STM) in ultrahigh vacuum and in ambient conditions.**

I. INTRODUCTION

With increasing miniaturization in many fields, especially in semiconductor engineering, new realms in terms of length scales have opened up. With every order of magnitude that systems scale down, new engineering techniques have to be developed.

In industrial chip manufacturing for instance, optical lithography will soon reach its physical boundaries. Also, in order to understand the basic processes and eventually develop groundbreaking new technologies based on quantum theory, even smaller length scales have to be made accessible.

"Making accessible" in this context means being able to control topographic, local electronic or even chemical properties of the material. A first step in this direction is changing the surface topography by irradiation with heavy keV energy ions in order to create surface defects. We have studied and compared surface defects on conductor, semiconductor and insulator surfaces.

An important way of producing nanometer-scaled structures (nanostructuring) on surfaces is kinetic sputtering by fast ions. Potential sputtering (PS), i.e, desorption induced by the potential energy of relatively slow multiply-charged ions (MCIs), holds great promise for more gentle nanostructuring [1, 2]

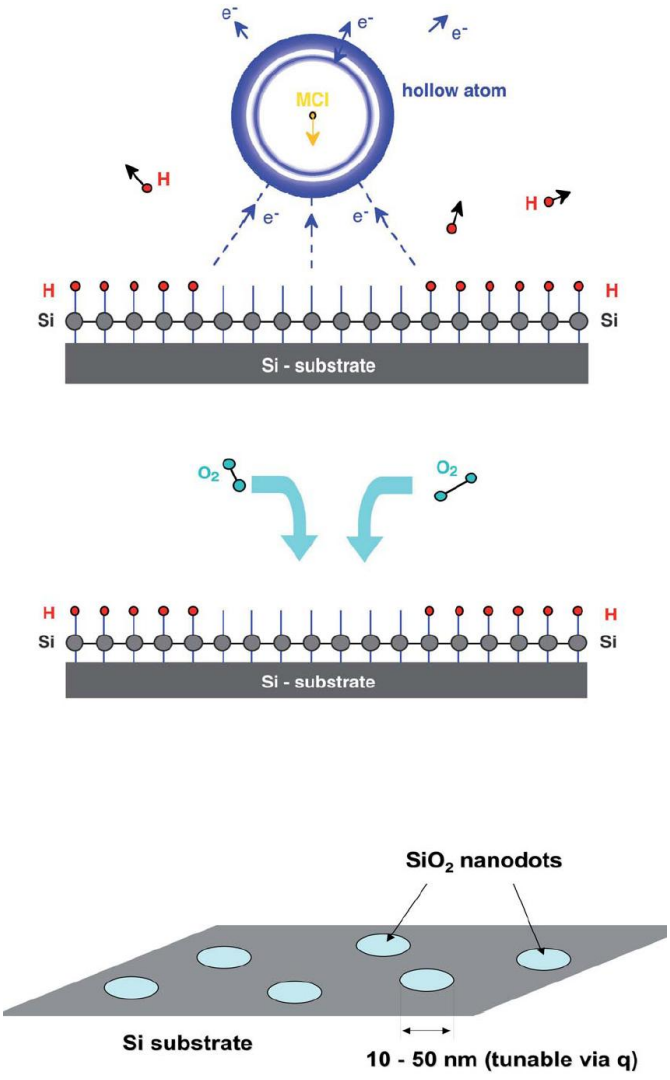

Fig. 1. SiO_2 nanodot formation on silicon.

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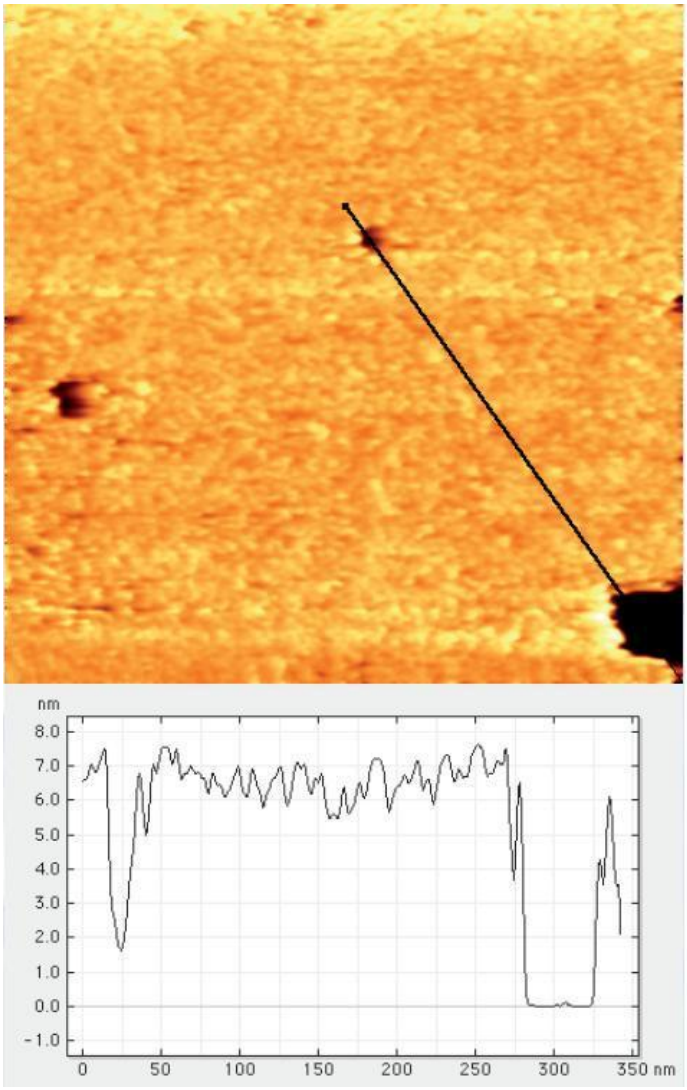

Fig. 2. SiO_2 nanodot formation on silicon. H-terminated silicon (111) was irradiated with Ar^{9+} ions (kinetic energy 45 keV, dose 10^{10} ions/cm^2) and subsequently oxidized. UHV STM reveals apparent depressions, resulting either from actual pits or an oxide layer with reduced tunnelling ability.

It can cause high sputter yields even for such low ion impact energies where kinetic sputtering and defect creation in deeper layers is not possible. While the physical mechanisms of PS have been the subject of extensive investigation (see [1, 2] and references therein), technical applications of slow MCIs have so far remained largely unexplored, despite the fact that slow MCIs provide unique opportunities for etching, ultra-thin film growth and nanostructure fabrication.

We are investigating whether beams of slow singly- or multiply-charged ions can be used effectively for nanostructuring [3, 4, 5, 6]. Currently, our two main approaches are to apply either high doses of singly-charged ions (in the range of 10^{17} ions/cm^2) or low doses of multiply-charged ions (in the range of 10^{10} ions/cm^2) followed by AFM and STM to visualize the effects of ion impacts.

The nanostructures induced by the ion bombardment of various semiconductor and insulator surfaces are studied under inert atmospheres or in reactive gas, in order to modify the surface around the ion impact sites. We investigate the size of any produced structures and attempt to achieve control by varying the MCI impact conditions (i.e. ion species used, charge state and kinetic energy). The investigations are carried out with AFM and STM techniques working under both UHV and ambient conditions (instruments: Omicron UHV AFM/STM, Asylum research ambient AFM/MFM MFP-3D).

For high dose singly-charged ion impacts various models exist that try to explain changes in surface morphology. For instance, the Bradley-Harper model [7] and its nonlinear extensions account for the formation of ripples and self-organised dot-structures (structures of hillocks) on amorphous surfaces [8, 9] or surfaces that are locally amorphized due to ion impact [10]. Smaller doses or even single ion impacts might produce other, different structures, ranging from small hillocks to craters, that are dependent upon the target material and its crystalline structure (Figs. 1 and 2). An effect that is always expected is the accumulation of defects at lattice steps (mono- or polyatomic steps on a crystal surface). This effect is clearly observed in experiments where graphite was irradiated (Fig. 3). At higher doses (above 10^{16} ions/cm^2) other effects such as smoothing or roughening of the surface can appear.

In this contribution we discuss the present status of our project.

II. Materials and Methods

Unlike in many other experiments of this kind, a 14.5 GHz ECR ion source was used to produce the ions irradiating the surface. With argon gas in the source, charge states of up to Ar^{10+} can easily be reached. The ions are extracted from the plasma with an extraction electrode at high potential, defining the kinetic energy of the ions. After the ion beam is focused by two magnetic quadrupoles, ions of a specific mass-to-charge ratio are selected using a sector magnet. Then the ion beam is focused and directed onto the target by various sets of deflection plates and electrostatic lenses. The relatively small energy spread of the extracted ions (tens of eV) and the specific mass-over-charge selection guarantee well-defined irradiation conditions.

For the rather exploratory measurements on highly orientated pyrolytic graphite (HOPG) and LiF we used Ar^+ ions with a kinetic energy of 5keV and a high ion dose of approximately 10^{17} ions/cm^2. With hydrogen-terminated silicon, a variety of measurements has been carried out, not only varying the particle's energy, but also the charge state and irradiation dose. The HOPG and LiF targets were prepared by cleaving under atmospheric conditions, while the hydrogen terminated silicon surface was produced by etching doped silicon (111) samples for 15 minutes in ammonium fluoride solution.

STM images of the irradiated surfaces in vacuum and AFM images in air were collected. The cantilevers for the AFM investigations are commercially available Olympus Si_3N_4 cantilevers with spring constants of 42 N/m. Imaging was performed in intermittent contact mode.

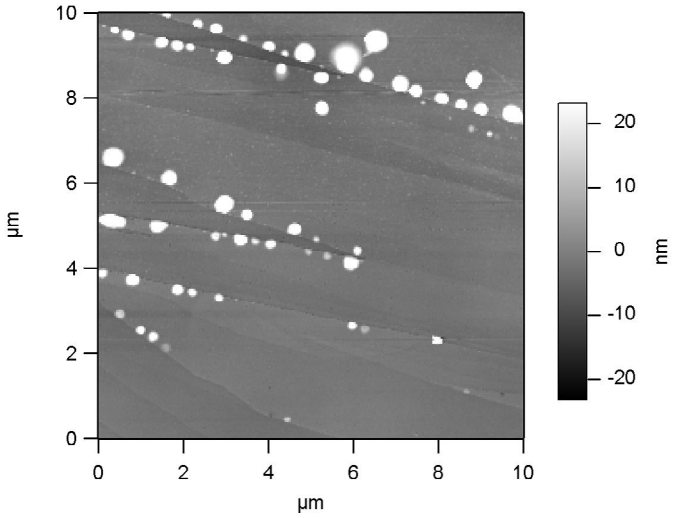

Fig. 3. HOPG irradiated with Ar^+ ions (kinetic energy 5 keV, dose 10^{17} ions/cm^2) imaged with ambient AFM in intermittent contact mode. The nanodefects aggregate on the steps of the substrate. Before irradiation only mono- or polyatomic steps are visible, but no nanodefects.

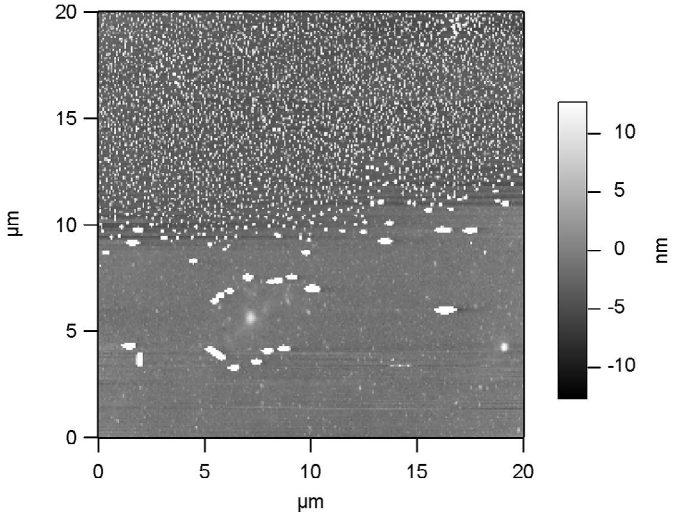

Fig. 4. H-terminated silicon irradiated with Ar^+ ions (kinetic energy 5 keV, dose 10^{17} ions/cm^2) imaged with ambient AFM in intermittent contact mode. The border region between irradiated (top) and not irradiated silicon (bottom) is clearly visible.

III. Results

Before ion irradiation, the samples are flat and atomically clean. Irradiation and subsequent UHV AFM/STM investigation takes place without breaking the vacuum: our home-built vacuum suitcase allows for sample transport from the ion source to the AFM chamber without exposing the samples to air.

After irradiation with MCIs, we see some raised areas in the UHV AFM images of silicon (data not shown). It is known that dangling Si bonds appear higher than a surrounding hydrogen-terminated surface in STM and we suspect that such features are just that.

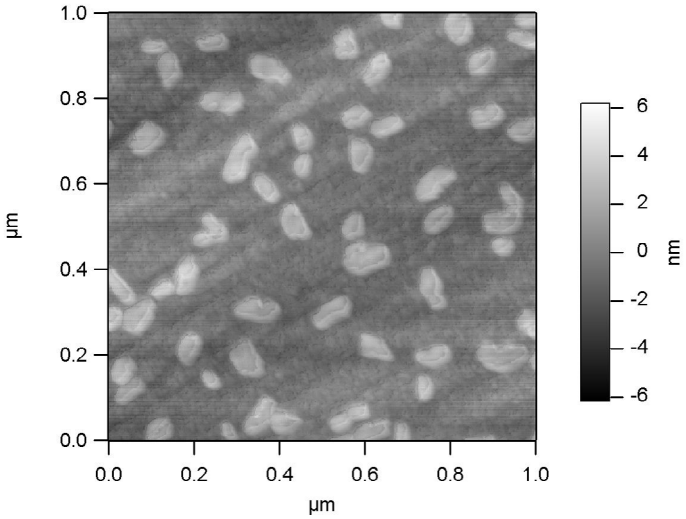

Fig. 5. LiF irradiated with Ar^+ ions (kinetic energy 5 keV, dose 10^{17} ions/cm^2) imaged with ambient AFM in intermittent contact mode. Before irradiation only mono- or polyatomic steps are visible, but no nanodefects.

At 45 keV impact energy, kinetic sputtering effects largely occur in deeper layers, away from the surface. The removal of hydrogen induced by the incoming MCI takes place before the impact. The argon then strikes the surface in the hydrogen-free area but does not disrupt the surface, leaving dangling bonds.

Oxidation afterwards results in features that appear to be lower in the STM images (Fig. 2). These features might be actual pits or an oxide layer (with reduced tunnelling ability).

Figure 2 shows the H-terminated silicon surface that was irradiated with low dose Ar^{9+} and subsequently oxidized. The ions used in these experiments were 45 keV Ar^{9+}. The dose was $1x10^{10}$ impacts per square centimeter. Oxidation was carried out by direct-current heating in an oxygen atmosphere (2 W for 15 minutes in 10^{-6} mbar O_2).

Currently, our focus is on improving the etching method used to obtain atomically-flat hydrogen-terminated silicon. This is generally known to be difficult. We have carried out extensive tests and believe the type of silicon we use is limiting our abilities. While we use atomically flat silicon as substrate, after hydrogen termination the flatness of our samples is not satisfactory. This property of course limits the explanatory power of the UHV STM results. Further studies are underway.

HOPG irradiated with Ar^+ ions (kinetic energy 5 keV, dose 10^{17} ions/cm^2) imaged with ambient AFM in intermittent contact mode is shown in Fig. 3. The aggregation of the ion-induced nanodefects on the graphite steps can clearly be seen. Before irradiation only mono- or polyatomic steps are visible on HOPG, but no nanodefects.

Ambient AFM work on H-terminated silicon irradiated with Ar^+ ions (kinetic energy 5 keV, dose 10^{17} ions/cm^2) clearly reveals the transition region between irradiated (Fig. 4 top) and not irradiated silicon (Fig. 4 bottom): ion induced nanodefects occur only in the irradiated part of the sample. The border is very distinct.

Ambient AFM work on freshly cleaved LiF irradiated with Ar^+ ions (kinetic energy 5 keV, dose 10^{17} ions/cm^2) is shown in

Figure 5. Before irradiation only mono- or polyatomic steps are visible, but no nanodefects (data not shown).

IV. Discussion, Conclusions and Outlook

In summary, distinct effects of ion bombardment were detectable on the surfaces investigated.

The high-dose work using singly-charged ions has afforded us better understanding of our equipment but it is not yet clear why the defects observed are so similar in size to those using higher energy MCIs.

A previous study on nanoscopic surface modification by slow ion bombardment performed on Al_2O_3 shows distinct correlations between height and width of nanodefects with the charge state of the projectiles [3, 4].

Further systematic experiments to enhance our understanding of the parameters influencing the generation of the nanostructures as well as to explain the different effects detected are under way.

Acknowledgment

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