

Replicating Nanostructures on Silicon by Low Energy Ion Beams

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Abstract. We report on a nanoscale patterning method on Si substrates using self-assembled metal islands and low-energy ion-beam irradiation. The Si nanostructures produced on the Si substrate have a one-to-one correspondence with the self-assembled metal (Ag, Au, Pt) nanoislands initially grown on the substrate. The surface morphology and the structure of the irradiated surface were studied by high-resolution transmission electron microscopy (HRTEM). TEM images of ion-beam irradiated samples show the formation of sawtooth-like structures on Si. Removing metal islands and the ion-beam induced amorphous Si by etching, we obtain a crystalline nanostructure of Si. The smallest structures emit red light when exposed to a UV light. The size of the nanostructures on Si is governed by the size of the self-assembled metal nanoparticles grown on the substrate for this replica nanopatterning. The method can easily be extended for tuning the size of the Si nanostructures by the proper choice of the metal nanoparticles and the ion energy in ion-irradiation. It is suggested that off-normal irradiation can also be used for tuning the size of the nanostructures.

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1. Introduction

The development of large-scale fabrication methods for structured surfaces with feature sizes in the nanometer range is still a constant challenge in the nanotechnology community. An accurate control of the surface topography would have a great impact in the fields of materials science and nanotechnology. For example, it is well known in the biomedical materials research that the shape of a surface controls its interaction with biological components, as has been recently noted [1]. In order to bring new alternatives to this key issue, numerous strategies, such as electron-beam lithography, self-assembling methods, soft lithography and other techniques, have been designed. Each of these methods has advantages and disadvantages depending on the minimum feature size and the degree of ordering or the material to be used.

In particular, for the case of nanostructured metal surfaces, novel and interesting routes have been developed recently by ion sputtering. This interest arises from the particular modifications of properties of the nanostructured metal surfaces, such as tribological properties (wear) or their interaction with electromagnetic radiation, which could be used for developing diverse technologies [2, 3].

In other instances, a scanning probe like a scanning tunneling microscope tip [4] or an atomic force microscope cantilever [5] has been used to engrave features with nanometer resolution. A drawback of scanning probe nanolithography is the limited scan area, typically, in the micrometer range, over which the pattern can be engraved. Restructuring over extended surface areas has been obtained by laser irradiation of metal and semiconductor surfaces [6].

For large-scale fabrication of nanostructures on metal surfaces by ion sputtering, surface erosion has proved to be a very valuable and useful technique [7]. By this procedure nanodotted patterns and ripple structures along any desired direction can be achieved both on metals [8] and semiconductor surfaces [9]. Although the method has demonstrated itself to be a powerful alternative for producing accurate nanopatterns, it has the disadvantage of being aggressive (i.e. a single crystal must be eroded for preparing each nanopatterned surface), making the method unsuitable for serial fabrication. The crystalline quality of the nanostructures produced by the sputtering process is doubtful. Thus the direct use of these nanostructures may not be favourable. However, this nanostructural pattern may be transferred to produce nanostructures of other materials [9].

In order to obtain nanostructures of good crystalline quality self-assembly would perhaps be the chosen route in many cases. For example, in spite of the indirect band gap of bulk Ge, Ge islands embedded in Si layers can be used for light emission [10]. Electron-hole pairs are captured in Ge islands and recombine by light emission. The necessary size to achieve confinement effects at room temperature is only a couple of nanometers. This size is at the limits of conventional lithography. An alternative is the self-assembly of 3D islands during the heteroepitaxial growth of Ge on Si. Elastic strain in the growing Ge layer drives the Ge island growth thereby causing partial strain

relaxation. The alloy material Si_xGe_{1-x} offers the possibility of band-gap engineering. However, when a Si_xGe_{1-x} thin film is grown on Si, unlike Ge the island growth does not occur, rather a relatively thicker uniform layer grows. Dense nanoscale islands of Si_xGe_{1-x} can still be produced by the method we propose and demonstrate in this paper.

In this report we show that by ion irradiation technique it is possible to tune the surface morphology on the nanometer scale that is in conformity with the strategy of using irradiation techniques for producing large-scale nanopatterned surfaces.

Our scheme of replicating nanostructural patterns on Si substrates is illustrated in figure 1. First self-assembled metal nanoparticles are grown on a Si substrate [figure 1(a)] by vacuum deposition of thermally evaporated metal atoms. This is followed by low energy ion beam irradiation. When the ions impinge on the empty surface (i.e, between the interisland space) they amorphize Si upto a depth comparable to the ion range in Si. However, when the ions impinge on a metal island they pass through the island and lose energy and consequently cannot penetrate deep into the underlying Si. As a result the thickness of amorphous Si under the metal islands is smaller. Thus amorphous Si (and complementarily crystalline Si) in the near-surface region of the substrate develops a pattern [figure 1(b)]. The amorphous Si is etched out. The etching process is carried out in an ultrasonic bath so that the metal islands are ejected and removed simultaneously leaving a crystalline nanostructured Si [figure 1(c)]. The feature size of the nanostructures can be reduced either by reducing the size of the metal islands for normal implantation or by irradiation at an angle with respect to the surface normal while providing an azimuthal sample rotation around the surface-normal as illustrated in figure 2.

2. Experimental procedure

Single crystal n-type Si(100) wafers were used for the replica nanopatterning. Before thin film (nano island film) deposition on Si, the substrates were cleaned sequentially in ultrasonic baths with methanol, trichloroethylene, methanol, deionized water and acetone. The native oxide on Si was not removed. The metal (Ag, Au, Pt) films were prepared by a conventional vacuum evaporation and an e-beam evaporation technique. An evaporation chamber was initially evacuated to below 1×10^{-6} mbar. Ag and Au metals (99.99 % purity) were then vapour-deposited from a resistively-heated molybdenum boat. The pressure during the vapour deposition process was kept at 2×10^{-6} mbar, and the thickness of the deposited Ag and Au was 2 nm as monitored by a quartz crystal microbalance with a deposition rate of 0.01 nm/s. The e-beam evaporation of Pt was done at a base pressure of 4×10^{-7} mbar. The thickness of the deposited Pt was 2 nm. The amount of metal deposited on the Si surface was also verified by Rutherford backscattering spectrometry experiments. The thermal deposition of Ag and Au and the e-beam deposition of Pt were carried out at room temperature of the substrate. Surface free energies of the metals being much larger than that of the native

oxide on the Si surface, island growth occurs upon metal deposition.

Ion irradiation was carried out with 32 keV Au^- ions with a fluence of 1×10^{14} ions/cm² at normal ($\sim 0^\circ$) as well as off-normal ($\sim 60^\circ$) angle of incidence. A uniform irradiation was achieved using a 1cm \times 1cm scanned beam. The incident ion current was kept between 40 nA and 60 nA. Such irradiation results in penetration of the Au^- ions into Si, Ag, Au and Pt film under normal incidence, up to 23.4, 7.9, 5.6 and 5.0 nm respectively as obtained from SRIM 2003 range calculation [11].

Following ion irradiation, the native oxide and the irradiation-induced amorphous Si were etched in HF (48%) in an ultrasonic bath. Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM-2010 (UHR) microscope operating at 200 keV. TEM specimens were prepared by mechanical thinning followed by ion-beam thinning with a Gatan precision ion polishing system with an accelerating energy of 3 keV.

3. Results

Ag, Au and Pt films of 2 nm nominal thickness on n-type Si(100) surfaces have been used for the present study. As the deposited metal grows as islands, height of each island is much larger than 2 nm. A native oxide of about 2 nm was present on Si in all the cases prior to thin film deposition. Figure 3(a) shows a cross sectional transmission electron microscopy (XTEM) image of an as-deposited Ag film. Ag islands, the Si substrate and the thin oxide between the metal islands and Si are seen in figure 3(a). For the as-deposited film, small Ag islands approximately 20 nm in diameter were uniformly observed on the Si(100) surface. Island growth is preferred when the interaction among the evaporated atoms (cohesion) is stronger than the interaction between evaporated atoms and atoms of the substrate (adhesion) [12]. In the island growth mode the size of the islands increases as the amount of deposited atoms increases, which has been observed and reported previously [13]. Figure 3(b) shows an XTEM image of Ag/Si thin film [similar sample as in figure 3(a)] irradiated with a fluence of 1×10^{14} ions/cm² at an impact angle of $\sim 0^\circ$ (normal incidence). Below the islands we observe dark irregular saw-tooth-like dark boundaries bounding crystalline Si. The lighter region below the islands and the native oxide is amorphous Si. The surface of the crystalline Si is patterned from the shadowing due to the metal islands. As the ions penetrate they have a lateral displacement component due to transverse straggling [11]. The shadowing is somewhat blurred because of transverse straggling of ions. However, the nanocrystalline features on the Si substrate have a one-to-one correspondence with the metal islands.

Figure 4(a) shows an XTEM image of a Ag/Si thin film irradiated with a fluence of 1×10^{14} ions/cm² at an impact angle of $\sim 60^\circ$. In this tilted angle geometry, the hillock patterns of crystalline Si are not directly under the islands. Figure 4(b) shows an XTEM image of an irradiated film etched in HF for 20 min. From figure 4(b) it appears that the amorphous Si has been etched in HF and Ag islands have fallen down into the

vallies between nano crystalline hillocks. The gap between the islands and the crystalline Si indicates that some oxide is still present and longer etching is required for complete removal of oxide. In addition, to remove these islands from the surface we performed the HF etching in an ultrasonic bath for 30 min. The XTEM image of this sample is shown in figure 4(c). Here the Ag islands are absent and only nanocrystalline Si hillocks are present on the surface. Figure 4(d) is the magnified portion of the Si substrate marked by a rectangle in figure 4(c) showing a high resolution (HR) XTEM image. The lattice resolution image in figure 4(d) shows the boundaries of nanocrystalline hillocks.

Figure 5(a) shows an XTEM image of an as-deposited Au film. Here the particle size is smaller (~ 10 nm) than in the case of Ag. Figure 5(b) and 5(c) show XTEM images of Au/Si thin films irradiated with a fluence of 1×10^{14} ions/cm² at impact angles of $\sim 0^\circ$ and $\sim 60^\circ$ respectively. Figure 5(d) is a HR-XTEM image of the magnified portion of the Si substrate marked by a rectangle in figure 5(b). A prominent nanocrystalline Si hillock is observed in this lattice image. In figures 5(b) and 5(c), we also notice the embedding of Au islands into Si. We observed similar features in MeV ion irradiation, where embedding of Au islands was more prominent compared to Ag islands. Additionally, embedded Au islands reacted with Si to form gold-silicide [14]. The embedding was also more prominent at 60° ion impact angle compared to 0° as observed here. As the ions penetrate a smaller depth for 60° -impact compared to 0° -impact, the amorphous Si layer is thinner in figure 5(c) compared to that in figure 5(b).

Looking at figure 3(a) and figure 5(a), where the island heights are typically ~ 20 nm and ~ 10 nm, respectively, the island density appears to be too high to be consistent with a nominal thickness of 2 nm. However, there is no inconsistency. When looked from the top [see figure 7(a)], the islands actually cover a small fraction ($\sim 25\%$) of the surface. In the cross-sectional view, such as in figure 3(a) and figure 5(a), islands at different lateral positions along the depth (i.e., perpendicular to the plane of the figure) are also visible. That is why island density appears to be high in the XTEM images such as figure 3(a) and 5(a). This is also the reason why overlapping islands with varying contrast are seen. Actually a Si hillock is formed under each metal island seen in the plan-view image like figure 7(a).

For normal incidence irradiation, crystalline Si hillocks are formed directly under the metal nanoparticles, as seen in figure 3(b). For tilted ion incidence the Si crystalline hillocks are laterally displaced compared to the metal particles that produce these Si hillocks by shadowing, as in figure 4(a). This is expected as illustrated in figure 2(b). In order to produce smaller Si hillocks, by tilted incidence, according to the scheme proposed in figure 2, the substrate has to be rotated around the surface normal during irradiation. We could not try this method as we do not have the facility for substrate rotation in our irradiation chamber. However, as we proposed in the last paragraph of section 1, there is another way to produce nanostructures of smaller sizes. That is, by making the deposited metal particles smaller. This can, in principle, be done by choosing a metal of higher surface free energy so that the surface free energy difference between the metal and the substrate is larger. We choose Pt for this purpose and the

results are discussed below. (Earlier we have used this concept of surface free energy difference to grow Ge nanoparticles on polymer-coated Si substrates [15]).

Figure 6(a) shows an XTEM image of an as-deposited Pt film. Here the particle size is much smaller (~ 2 nm) than in case of Ag and Au. Here the lattice image of crystalline Si and the native oxide layer between the islands and crystalline Si are clearly seen. Figure 6(b) shows a HR-XTEM image of the film shown in 6(a) following ion irradiation with a fluence of 1×10^{14} ions/cm² at an impact angle of $\sim 0^\circ$ and HF etching in ultrasonic bath for 30 min. A nanocrystalline Si hillock of ~ 6 nm diameter is seen in the lattice image of figure 6(b). This sample in figure 6(b) shows a reddish tinge when exposed to ultraviolet light of 275 nm wavelength. It is known that Si nanoparticles can emit red, green, blue light emission depending on the particle size [16]. A 6 nm diameter Si particle is expected to emit red light [16].

For Ag, Au and Pt nanoparticles grown on the native oxide layer atop the Si substrate, we notice a general trend — Ag islands are the largest and the Pt islands are the smallest. This may be understood from their respective surface free energies. The surface free energies of Ag, Au and Pt are 1.25 J/m² [17]), 1.55 J/m² [17]) and 2.55 J/m² [17] respectively. Consequently the largest difference in surface free energy between Pt and the native oxide (0.3 J/m² [18]) on which it is growing is apparently responsible for the growth of smallest islands in the case of Pt. For a given metal, the size of the islands can be controlled by controlling the substrate temperature during deposition [19].

Spherical monodisperse nanoparticles of much smaller average size, compared to what is shown here, can be prepared by ion beam sputtering of samples like those shown in figure 3(a) and 5(a). Upon irradiation, nanoparticles are ejected from those on the substrate [19, 20]. When these sputtered particles are captured on a Si wafer and this Si wafer with smaller nanoparticles is used for replicating nanostructures by the method described here, much smaller nanostructural patterns can be created on Si. We have prepared Au nanoparticles of an average diameter of ~ 5 nm on catcher Si wafers during ion sputtering of samples such as that shown in figure 5(a). An example of this is shown in figure 7. The ejected Au particles are much smaller than the size of the original deposited Au particles. More details of this aspect will be presented elsewhere [21].

A way to obtain further smaller Si nanostructures from, say, those in figure 6(b) is to let it be oxidized. Assuming the same oxidation behaviour of Si wafers and Si nanocrystals, ~ 2 nm thick native oxide will form along the outer boundary of the nanocrystal. This would reduce the diameter of the Si nanocrystalline features from ~ 6 nm to ~ 2 nm, which is expected to emit light of shorter wavelength — close to blue light [16].

Pyramid- and dome-shaped self-assembled quantum dots of Ge grows on Si following the Stranski-Krastanov growth mode [22]. Ge islands grow on three atomic layers of uniform Ge. However, Si_xGe_{1-x} layers grow on Si uniformly to much larger thicknesses depending on the composition (the value of x). Si_xGe_{1-x} nanostructures can

be produced from this uniform Si_xGe_{1-x} layer. In order to obtain Si_xGe_{1-x} nanoislands on Si, the method presented here can be conveniently used provided an appropriate etchant is found for amorphous Si_xGe_{1-x} . This would provide a wider tunability of optical devices using Si_xGe_{1-x} as the band gap of Si_xGe_{1-x} is tunable over a wide energy range.

For optoelectronic applications the quantum yield of the Si nanostructures is of great importance. The aspect of quantum efficiency, which has not been addressed here, is to be explored in future work.

4. Conclusions

Here we have proposed and demonstrated a method of replicating nanostructures on Si surfaces using metal nanoparticles on Si as mask and low energy ion-irradiation. Although the nanostructures on Si are not exact replicas of the overlying metal islands there is a one-to-one correspondence. When the metal islands are small enough the features of nanocrystalline Si replicated on the Si surface are also small - small enough to show optical emission within the visible band. With a proper choice of etchant the method can be used for a larger number of substrates besides Si. Although HF does not etch crystalline Si, here we have found that amorphous Si can be effectively etched in HF.

5. Acknowledgments

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Figure captions

Figure 1. Scheme showing the different steps involved in the replica nanopatterning method with the ion beam incident along the surface-normal direction. (a) Metal nanoparticles on Si, (b) ion irradiation and creation of patterned amorphous Si, (c) after etching out amorphous Si, nanostructures of Si are revealed.

Figure 2. Illustration of how smaller nanostructures on Si can be produced by tilted implantation and azimuthal rotation of the substrate. (a) Metal nanoparticles on Si, (b) normal irradiation (left), off-normal irradiation with azimuthal rotation (right), (c) larger and smaller Si nanostructures corresponding to the cases in (b).

Figure 3. XTEM images: (a) As-deposited Ag nanoisland film; a thin (~ 2 nm) native oxide layer between Ag islands and crystalline Si is seen, (b) Ag film in (a) irradiated with 32 keV Au^- ion at a fluence of 1×10^{14} ions / cm^2 with the ion beam incident along the surface normal (0° impact angle). The structures formed underneath the Ag islands have a one-to-one correspondence. An amorphous Si layer (~ 20 nm thick) is formed between the Ag islands and the underlying crystalline Si.

Figure 4. XTEM images: (a) The film in 3(a) irradiated with 32 keV Au^- ions at a fluence of 1×10^{14} ions / cm^2 at 60° impact angle, (b) the irradiated sample in (a) etched in HF for 20 min; the amorphous Si layer between Ag islands and the crystalline Si is now thinner, (c) the sample in (a) etched in HF for 30 min in an ultrasonic bath; the islands, the native oxide, and amorphous Si are removed, (d) the lattice image of a magnified portion of the image shown in (c) marked with a rectangle.

Figure 5. XTEM images: (a) An as-deposited Au nanoisland film, (b) the Au film in (a) irradiated with 32 keV Au^- ions at a fluence of 1×10^{14} ions / cm^2 at 0° impact angle, (c) the Au film in (a) irradiated with 32 keV Au^- ions at a fluence of 1×10^{14} ions / cm^2 at 60° impact angle, (d) the lattice image of a magnified portion of the image shown in (b) marked with a rectangle.

Figure 6. XTEM images: (a) An as-deposited Pt nanoisland film; below the Pt islands the sharp native-oxide/Si interface is seen, (b) the Pt film in (a) irradiated with 32 keV Au^- ion at a fluence of 1×10^{14} ions / cm^2 at 0° impact angle and then etched in HF for 30 min. in ultrasonic bath. The lattice image of a Si island (~ 8 nm height and ~ 7 nm diameter) is seen. The sharp flat Si interface in (a) is nanostructured as shown in (b) by the ion-beam replica nanopatterning method.

Figure 7. Plan-view TEM images of an (a) as-deposited Au nanoisland film (nominal thickness 1.3 nm) on Si and (b) of ejected Au islands collected on a catcher Si wafer during ion irradiation (1.5 MeV Au²⁺ ions, fluence : 1×10^{14} ions/cm²) of the sample in (a). (c) and (d) show island (lateral) size distributions for the cases in (a) and (b) respectively. The most probable size (diameter) in (c) is ~ 11.5 nm (Gaussian fit) and that in (d) is ~ 4.5 nm (log-normal fit).

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