Ordered nanocrystals on argon ion sputtered polymer film

Qiangmin Wei a, Jie Lian b, Sha Zhu c, Weixing Li a, Kai Sun a, Lumin Wang a,c,*

a Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA
b Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA
c Department of Nuclear Engineering and Radiological Michigan, University of Science, Ann Arbor, Michigan 48109, USA

Received 9 October 2007; in final form 10 December 2007
Available online 28 December 2007

Abstract

We demonstrate that a variety of intriguing patterns can be induced by several keV Argon ions on the ultrathin polymer films at glancing angles of incidence with the simultaneous sample rotation. These periodic structure films can be used as the templates to fabricate densely packed nanometer-scale structures by deposition of atoms. Well-ordered arrays of stripe-like Si nanostructures with 7 nm wavelength and uniformly sized and shaped nanoparticles of copper in diameter of 7 nm were produced on the thin polymer film. This approach represents a convenient route for fabricating nanometer-scale wires and dots for metals and semiconductors.

© 2007 Elsevier B.V. All rights reserved.

Bombardment of solid surfaces with low energetic ions is under intensive investigations due to its self-assembly into well-ordered periodic structure. A variety of topographies can result from surface erosion depending on sputtering conditions and material properties with the wavelength scales of the order of 10–1000 nm [1–5]. Low energy ion bombardment is regarded as an alternative process for the fabrication of various nanostructured surface or interfaces besides common applications such as ion beam assisted deposition, reactive etching, sputter etching, and plasma assisted chemical vapor deposition [4,6]. Recently, it has been reported that hexagonal ordering quantum dots can be generated by Ar + ion sputtering under normal incidence on the GaSb and oblique ion incidence sputtering of InP with sample rotation [2,3]. Compared with the low throughput of serial lithographic methods, this novel approach opened a promising route for the fabrication of uniform semiconductor quantum dots ordered in a hexagonal array. In this Letter, we illustrate that ultrathin films can self assemble into ordered stripe like patterns upon low energetic ion bombardment and these films can be used as templates to pattern metal and semiconductor structures.

The polymer films containing 30% bisphenol-F epoxy resin, 65% tetrahydrofuran and 5% methyl ethyl ketone were used in the experiments. We first coated the dilute polymer solution on the 200 mesh (lines/inch) copper grid, and then annealed at different temperatures for 1 h for solidification. The ion bombardment experiments were carried out at room temperature in a commercial ion milling system with a pressure of $3 \times 10^{-3}$ Torr. 2–5 keV Ar + ions with flux of $10^{14}$ cm $^{-2}$ s $^{-1}$ at an angle of 80° from normal were used. After well-ordered patterns were induced by ion beam on the thin polymer film, we made deposition for copper and silicon. The sample was rotated during bombardment and deposition. The morphology and microstructure of coated films upon ion bombardment and deposition were measured by an analytical transmission electron microscope (TEM). Fig. 1 shows the procedure used to prepare well-ordered nanopatterned structure of metal and semiconductor from an ultrathin film.

The bright-field TEM images of a polymer film after bombardments by 4.2 keV Ar $^+$ ions at an angle of 80° from normal at different ion fluences with a constant speed of rotation are shown in Fig. 2. Before irradiation, no ordered features were observed, different from the well-ordered
diblock polymers which were widely used as template for nanofabrications [7,8]. The thickness of film is about 10–20 nm. At an ion fluence of $1 \times 10^{17}$ cm$^{-2}$, equivalent to an exposure time of 10 min, the sand like ripples with the wave length of 25 nm appear (Fig. 2a). Fig. 2a illustrates the special area that links the well-ordered patterns and plain surface, from which we can find that the stripes result from the diffusion of shorter chain molecules through the interactions among the ingredients induced by ion irradiation. It can be seen that polymers irradiated by low energy ions underwent the degradation by nuclear stopping in which chain scission, chain aggregation, and molecular
emission occurred [9–11]. These effects are due to the large amount of energy storage in the molecular environment, which overcomes the binding energies of organic molecules. At higher fluence, the nucleation and growth of clusters of amorphous carbon and radicals were generated, leading to the final structure that has little memory of original chain structure [12]. Two opposite effects occurred upon energetic ion irradiation of polymers [9]: one of which is related to crosslinking where two or more molecules were chemically joined by a covalent bond and second to a chain scission where the molecular bonds were broken and the overall chains were shortened. These two mechanisms correspond to the roughening and smoothing on the irradiated surface of bulk materials, respectively [2]. These formation and recombination of varieties of production induced by energetic ions in polymer films far from the equilibrium can contribute to the pattern formation, similar to the ordered semiconductor dots on the single GaSb surface induced by the ion irradiation [2]. With the increase of exposure time, the polymer films evolve into striped patterns (Fig. 2b). The defocus TEM images show the oriented stripes seem to consist of bundles of small voids produced by the interaction between the gas, radicals and small molecules induced by irradiation.

Another pattern with wavelength of 7 nm was also found on the same component of polymer films but at different annealing temperatures as shown in Fig. 2c and d. The variation in pattern wavelengths can be attributed to the diffusion of different length of chains of molecules in the films: the longer chains in polymer film have less mobility and thus leading to the shorter wavelength. High resolution transmission electron microscope (HRTEM) image (Fig. 2d) of the nanostructure induced by Ar$^+$ ions with the exposure time of 30 min shows that the high density of networks of molecule chains formed, and thus the diffusion of molecules became slower leading to the shorter wave length.

One interesting phenomenon observed on the irradiated polymer films is the nanostructures analogous to the patterns in the nature. Fig. 3 shows some of these patterns (the colors are added by using Photoshop) induced under different conditions. This emphasizes one of important points in the theory of pattern formation outside of equilibrium that similar patterns can occur in very different systems [13]. The different parameters (exposure time, ion energy, rotation of sample, pressure, boundary conditions, etc.) result in the variations of characteristics of patterns. For example, it shows that the higher speed of rotation, the shorter wavelength and better ordered patterns. The sand ripple shown in Fig. 3a is induced by the bombardment on the fixed samples with the energy of 4.2 keV for 20 min, while Fig. 3b–d were taken at the rotation of 6 rpm of samples.

Commonly observed microdomain morphologies on the surface of irradiated polymers, termed ripples, striations or corrugations, appear to be similar with these on the inorganic material surface, depending on material structure and irradiation conditions [14–17]. Modern understanding of pattern formation is the concept of instability in which a phenomenon goes under the name of dissipative structure [13,18]. The ion induced surface instability of solid is regarded as the superposition of interacting between the roughening instability and diffusion smoothing, which gives rise to waves propagating in different directions [1,2]. The pattern selection was determined by the state that grows fastest near the instability [13]. A widely accepted theoretical approach describing the pattern formation on amorphous substrates was proposed by Bradley and Harper in which the surface instability is described by curvature dependent terms and surface diffusion terms [1]. Nonlinear terms were taken into account in the development of this model by focusing on the roughening [19,20] and redeposition [21]. In our case, the ultrathin polymer films were suspended on the grid, in which the interaction of defects with the adjacent neighbors of molecules can influence the diffusion coefficients [22].

![Fig. 3. Complex patterns observed in thin film. These images are analogous to the patterns in nature but on nanometer scale. (a) Ripples induced by ion beam at the energy of 4.2 keV up to fluence of $5 \times 10^{16}$ cm$^{-2}$ analogous to sand ripples in nature. (b) Fingerprints-like patterns induced by ion beam with the rotation of sample at the speed of 6 rpm. The energy is 4.2 keV and the fluence is $2 \times 10^{17}$ cm$^{-2}$. (c) Leaf-like structures induced by ion beam on the films with the rotation speed of 6 rpm. The energy is 5 keV and the fluence is $6 \times 10^{17}$ cm$^{-2}$. (d) Worm-like structures induced by ion beam with the same preparing conditions as those in (c) but with different boundary conditions.]
induced by the irradiation is different from this on the surface of bulk materials previously studied. By considering the nature of the effects of irradiation on the thin polymer film, it can be concluded that the main terms determining the formation of the well uniformly ordered patterns are ascribed to the interaction of defects induced in the polymer films by the ion irradiation. Generally, for bulk materials (for example, semiconductors, glass, and insulators), particles instead of ripples can be induced under the condition that whole substrate is irradiated during rotation. However, if only a part of the substrate is irradiated by a focused ion flux such as a line beam or a spot beam, then a circular-ripple pattern would develop [22,23]. Our experiments are performed under this condition. The straight lines can be considered as circles with very large radius.

With respect to the potential application of this technique, we can use these thin patterned films as templates to fabricate the well-ordered metallic and semiconductor nanostructures. Due to these ordered patterns come from the interaction of defects, they can provide the nucleation sites for the diffusion atoms, thus leading to the transfer of the patterns to the deposited materials. In order to move into their preferred nuclear sites before they aggregate into spherical shape on the normal surface, a high velocity of diffusion for the deposited atoms was needed. We deposited copper and silicon atoms, for example, on these ordered materials and found that structures of nanocrystals formed on the film exactly follow the existing patterns (Fig. 4). For deposited silicon atoms, well-ordered arrays of silicon with wavelength of 7 nm are observed (Fig. 4a). These nanolines consisting of deposited atoms are found to be polycrystalline (Fig. 4b), made of grains that generally extended across the full length of the striped patterns on the polymer film. The occupied stripes on the polymer films correspond to the defect domains, while the amorphous polymers ~2 nm wide distributed among these nanolines is related to the perfect domains of polymer film. Compared with the structure formed by deposited silicon atoms in Fig. 4a and c reveals that the nuclear domains for preferential nucleation sites are periodic structures with two different widths: 7 nm and 25 nm corresponding to the wavelength of Fig. 2b and c. When the spacing among these curves became uniform under the suitable irradiation conditions, we obtain the perfect lattice structure of silicon in Fig. 4a.

Fig. 5 shows the copper dots on the polymer film with the diameter of 7 nm equal to the wavelength of silicon stripes. Short range ordering can be found from the image and corresponding the corresponding two-dimensional autocorrelation. The HRTEM image in Fig. 5b reveals the polycrystalline structure of copper dots. In order to quantitatively determine the size of dots and ordering, the average power spectral density (PSD) of the sample surface (the surface height–height autocorrelation function) is calculated (Fig. 5c) [24]. The first peak in the PSD graph gives a mean dot size of approximately 7 nm. The multi peaks are also visible indicating the short ordering and size homogeneity of dots. The formation of copper dots can be attributed to the preferential nucleation of atoms on the patterned thin films. As it shows in Fig. 2c, at the beginning of ripples formation, the stripes induced by ion beam are composed of bundles of small voids. The deposited atoms can preferentially select these voids to nucleate and form dots. The thickness of the deposited Cu and Si layers is about 20–30 nm.
In summary, our experiments describe a method for creating well-formed patterns through self-organization on the thin films by irradiation. Using these films as templates well-ordered metal and semiconductor nanowires can be fabricated by nucleation of deposited atoms on the preferential sites. It is suggested that nanopatterns induced by ion beam on the polymer films before deposition are composed of high density defects, which provide the aggregation regime for randomly deposited atoms, thus leading the deposited atoms to nucleate selectively inside these regions and producing well organized nanostructures. This approach illustrated a convenient route for fabricating nanometer-scale surface patterns for metals and semiconductors, which may have the potential applications for specific device.

Acknowledgements

This work was supported by the Office of Basic Energy Science of the US Department of Energy through Grant No. DE-FG02-02ER46005.

References


Fig. 5. The structure of deposited copper dots on the thin polymer film. (a) Copper dots on the thin polymer film. Inset is the corresponding two-dimensional autocorrelation showing the regularity and hexagonal ordering of the dots. (b) HRTEM image of copper dots. (c) Angular averaged power spectral density (PSD) obtained from (a). The peak shows the mean size of dot structures.