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Formation of ordered nanodroplet chains on a solid surface by enhanced surface diffusion and shadow effect

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ABSTRACT

We report on a mechanism that under an off-normal incident ion beam, ordered nanodroplets may emerge spontaneously from a flat solid surface and line-up into chains perpendicular to the beam direction, forming a highly ordered hexagonal pattern. This behavior is in contrast to the general belief that an off-normal bombardment produces surface ripples, while the formation of dots requires either normal bombardment or off-normal bombardment with simultaneous sample rotation. The self-assembled nanodroplets reveal a mechanism different from the usual sputtering process. We propose a continuum theory which shows that the balance of mass flux plays an important role for the hexagonal pattern formation while the shadow effect causes the droplets to align into chains. The simulations suggest that the fundamental mechanism may be applicable to other systems, which may lead to an effective approach for nanofabrication.

1. Introduction

Self-assembled nanodots have wide applications from advanced materials to electronic and optical devices. To date, two approaches are largely studied for self-assembled dot formation on a semiconductor surface using an ion beam: normal bombardment and off-normal bombardment with simultaneous sample rotation. Re-deposition of sputtered particles is known to cause regular dot formation in the former approach [1]. The latter extends a well-known phenomenon that off-normal bombardment can generate ripples on a surface [2]. The sample rotation at off-normal bombardment has the same effect of normal bombardment by time averaged etching in all directions. Since the discovery of spontaneous dot formation during ion beam bombardment [1], various semiconductors including GaSb [3], InP [4], Si [5,6], and InSb [7] have been investigated to enhance the regularity, or to study the effect of parameters such as the angle [8,7], fluence [9] and temperature [4,10] on the morphology.

It has been observed that preferential sputtering leads to dot formation during ion bombardment on semiconductor compounds such as GaAs [11–13] and InP [14]. Small dots under preferential sputtering usually appear as droplets. For example, when a GaAs substrate is bombarded, the element As is more likely to be sputtered away, leaving a surface layer composed mostly of Ga. Due to the low melting point of Ga atoms, they are highly mobile near room temperature. These Ga atoms diffuse on the surface and nucleate, forming pure Ga droplets. The size and location of droplets under preferential sputtering are usually random. However, an ordered pattern can be obtained on a pre-patterned surface using preferential sputtering. The pre-patterned nanoscale holes act as nucleation sites for the droplets to form at these locations [15,16].

A recent experiment of off-normal bombardment on a GaAs substrate with a Ga ion beam showed an intriguing finding [17]. Ga droplets with sizes from 25 to 70 nm in diameter on the GaAs surface self-assembled into a highly ordered hexagonal pattern. These droplets moved toward the beam and lined up into chains perpendicular to the projected ion beam direction, showing that ordering was independent of the orientation of the substrate. This is an interesting observation since regular dots formed at off-normal bombardment without substrate rotation. It is well-known that close to the melting point, Ostwald ripening or coalescence often leads to nonuniform particle sizes during particle growth. Here, this normal physical behavior was hindered under low energy ion bombardment, and highly ordered and uniform hexagonal patterns were induced.

Most models of ion bombardment are based on the theory of Bradley and Harper (BH) [18], which explains surface roughening by the curvature-dependent instability; valleys are more likely to be sputtered than tops because energies released from penetrated ions are more concentrated at the valleys. However, the mechanism of roughening during preferential sputtering on a GaAs substrate is different. The difference becomes clear when we compare the features of structures. The droplets formed under preferential sputtering are not densely packed and are amorphous. In contrast, the dots under usual sputtering are highly packed and partially amorphous [1]. In addition, the composition of the droplet is different from that of the

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substrate. These observations suggest that the surface roughening in preferential sputtering is caused by diffusion rather than etching, and the different materials between the droplet and the substrate make the wetting behavior significant.

Below we propose a continuum theory, showing that the high mobility and anisotropic supply of atoms play an important role for the hexagonal pattern formation, while the shadow effect causes the droplets to align into chains perpendicular to the direction of the incident beam. In particular, we aim to use a simple model to capture the most essential mechanism so that the approach may be applicable to other materials systems as long as the key effects are there.

2. Modeling

We represent the substrate surface with a spatially continuous and time dependent function, $h(x,y,t)$, where x,y are axes parallel to the substrate surface and t is time. Starting from a flat surface, the formation of surface morphology and its evolution is captured by the change of h in the z direction. Take the GaAs system as an example. Preferential sputtering generates a very thin layer of Ga on the GaAs substrate. Our model aims to capture the evolution of this thin layer of Ga film under continuous mass supply by sputtering of the substrate, diffusion on the surface, shadow effect, and the effect of substrate wetting. The x–y axes move with the substrate surface to discount the overall height change due to any uniform material removal under sputtering.

Kinetics plays an important role in many self-assembly systems [19,20]. We consider concurrent surface kinetics including diffusion, sputtering and the supply of atoms. The time evolution of the surface is given by

$$\frac{\partial h}{\partial t} = -\nabla\cdot\mathbf{J} - \beta(\nabla h)^2 + \eta. \qquad (1)$$

The first term represents mass conservation, where $\mathbf{J}$ is the diffusion flux of Ga on the substrate. The second term, $\beta(\nabla h)^2$, describes slope-dependent sputtering of Ga atoms from a thin layer of Ga film [21], where β is a parameter dependent on the beam energy. The sputtering of Ga atoms happens more likely from the surface of a droplet ($(\nabla h)^2 \neq 0$) than from a flat surface ($(\nabla h)^2 = 0$). While there is a net supply of Ga atoms on the substrate surface due to the preferential sputtering of As, sputtering dominates on the surface of Ga droplets since there is no preferential sputtering there (no As in the islands). At off-normal bombardment, the droplet surface facing the beam may lose more material than the back side. However, the Ga droplets behave like liquid because of the low melting point near room temperature. The atoms on the droplets are highly mobile so that a droplet tends to quickly recover and keep the hemi-spherical shape as observed in the experiment. Therefore, the droplets appear to experience an effective isotropic sputtering and maintain their axial symmetrical shape. Thus we assume isotropic sputtering, and the lowest order term independent of the axis orientation is quadratic, or $(\nabla h)^2$. The third term represents the source of Ga atoms as a total effect of Ga supply from the substrate due to preferential sputtering of As, as well as deposition from the incoming Ga ion beam.

We find that the diffusion flux has a critical effect on the ordered hexagonal pattern formation. Fig. 1 illustrates the concept. Consider a droplet that is supplied by atoms from the left (Fig. 1a). This mass flux causes the droplet to expand to the left and grow larger (Fig. 1b). However, the sputtering of atoms from the droplet tends to reduce its volume. The droplet reaches a stable size when the two actions reach equilibrium. Thus, we will observe a droplet moving left with a stable size. Now consider a droplet with neighboring droplets. We can roughly say that the distance between two droplets represents the amount of Ga supply because Ga atoms are mainly

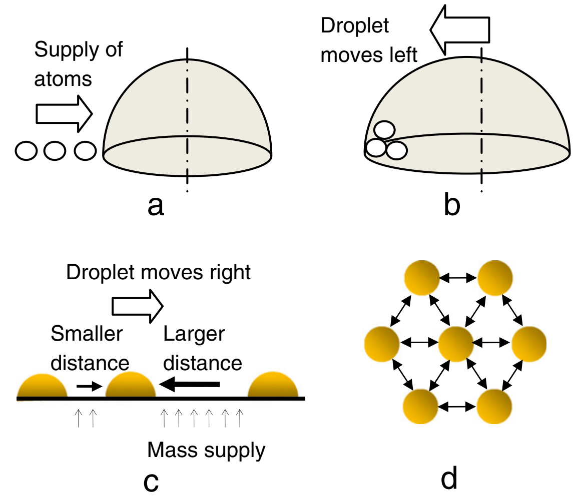

Fig. 1. Anisotropic supply of atoms leads to the formation of a hexagonal pattern. (a) Atoms are supplied from the left. (b) The droplet expands left and grows larger, while sputtering tends to reduce its volume. At equilibrium a droplet moves left with a stable size. (c) The larger distance between the middle and right droplets allows more differential sputtering and supply of atoms. Thus the middle droplet gets a net mass flux to the left and moves right, until it has the same distance to both droplets. (d) The stable configuration is a hexagonal lattice, where the distance between all the droplets in the lattice is the same.

supplied from the GaAs substrate due to preferential sputtering of As. In Fig. 1c, the droplet in the middle gets a net mass flux to the left because it has a larger distance to the right droplet than to the left one. As a result, it moves right until it has the same distance to both droplets. Now apply this mechanism to randomly distributed droplets. As the sputtering process continues, all the droplets tend to be separated by the same distance from all their neighbors. When the system reaches the equilibrium state, droplets will arrange into a hexagonal pattern (Fig. 1d).

In the following, we consider the actions that contribute to $\mathbf{J}$. The droplets are generated by nucleation and aggregation of diffusing atoms on the substrate surface. In the model, we represent the growth of droplets as an up-hill flow along the slope, which is $\alpha\nabla h$, where α is the growth rate that can be affected by the mobility of atoms. This term is motivated by instability in the deposition process: atoms deposited on a terrace tend to attach to the side of the upper terrace rather than stepping down to the lower terrace, which can be represented by an uphill flow [22]. Although the mechanism is not the same, an uphill current expressed by this lowest order term captures the growth of droplets due to the supply of atoms from their perimeter. The effect due to the surface and wetting energy is considered in the following way. The chemical potential of atoms can be expressed by $\mu = \mu_\gamma + \mu_w$, which includes the contribution from the surface energy, μ_γ and from the wetting energy μ_w. Atoms tend to move from regions of high chemical potential to regions of low chemical potential, giving $\mathbf{J} = -M\nabla\mu$, where M is the mobility [23,24].

The chemical potential due to the surface energy can be expressed by $\mu_\gamma = K\gamma\Omega$ [25], where K is the surface curvature, γ is the surface energy per unit area, and Ω is the atomic volume. The curvature can be expressed by the second derivative of the surface height, $K = -\nabla^2 h$. The wetting energy reflects the important effect of the substrate on the morphological evolution of a thin film on top of it. In the model we consider Ga atoms diffusing around on the substrate like a thin Ga film. The wetting energy is expressed as an exponentially decaying function of h with a singularity at $h \to 0$ [26],

$$\mu_w = -w_0\left(\frac{h}{\delta_w}\right)^{-\alpha_w}\exp\left(-\frac{h}{\delta_w}\right) \qquad (2)$$