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Surface science of plasma exposed surfaces: A challenge for applied plasma science

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A B S T R A C T

This article introduces a deterministic approach to using low-temperature, thermally non-equilibrium plasmas to synthesize delicate low-dimensional nanostructures of a small number of atoms on plasma exposed surfaces. This approach is based on a set of plasma-related strategies to control elementary surface processes, an area traditionally covered by surface science. Major issues related to balanced delivery and consumption of building units, appropriate choice of process conditions, and account of plasma-related electric fields, electric charges and polarization effects are identified and discussed in the quantum dot nanoarray context. Examples of a suitable plasma-aided nanofabrication facility and specific effects of a plasma-based environment on self-organized growth of size- and position-uniform nanodot arrays are shown. These results suggest a very positive outlook for using low-temperature plasma-based nanotools in high-precision nanofabrication of self-assembled nanostructures and elements of nanodevices, one of the areas of continuously rising demand from academia and industry.

1. Introduction

Surface science is a research field which deals with the structure, arrangements, kinetics, formation and other properties of few atomic layers of a solid near its interface with the environment [1]. Atoms in these layers (hereinafter called surface atoms for simplicity) are subject to very different conditions compared to their counterparts in the material bulk. Indeed, they face the environment and are the first to respond to any action exerted on the material by external atoms, molecules, radicals, electromagnetic fields, etc. In particular, the collective response of surface atoms to external actions determines whether the solid will accept external atoms and allow them to self-organize on the surface to form ultra-small nanoassemblies. This particular response strongly depends on the properties of the material itself, its surface, and is also strongly affected by the environment and its specific action. To understand the range of possibilities arising from the interaction between the surface and the environment, atomic description of surface processes based on diffusion and dynamic models is commonly used [1].

Surface science is known as one of the most delicate research fields which deals with the motion of individual adsorbed atoms (adatoms) along atomic-scale features on the surface and their self-organization into small clusters, islands, and other nanoscale objects. For this reason, small (typically submonolayer) amounts of adatoms are supplied to the surface and then traced by ultra-sensitive tools such as Scanning Tunnelling Microscopy (STM) [2], Atomic Force Microscopy [3], and several others. Furthermore, because of this delicate nature of atomic-scale surface processes, in most cases ultra-high-vacuum and "mild" (e.g., non-reactive) adatom creation and deposition environments are commonly used.

Despite very impressive recent advances in this area, self-organization on solid surfaces exposed to "harsh" environments still remains one of the main challenges of surface science. Low-temperature plasmas are good example of such an environment. However, understanding the way in which plasma-related effects such as the electric charge, ion fluxes, plentiful radicals, clusters and other reactive species, electric fields, polarization effects, etc. may affect the elementary surface processes studied by the surface science, still remains a major unresolved issue. Moreover, due to the overwhelming complexity of theoretical description and experimental investigation of elementary processes involved in plasma–surface interactions, plasma exposed surfaces are presently not in the spotlight of the surface science research. Plasma Nanoscience [4] is a research area, one of the major aims of which is to bridge the three-dimensional (3D) world of the physics of plasmas and gas discharges and the two-dimensional (2D) world of surface science and gainfully use this unique combination to synthesize exotic

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nanoscale assemblies and nanostructured materials with intricate electronic, optical, structural, thermal and other properties [4,5]. The latter aspect is of particular importance to applied plasma science. However, researchers working in this area also very rarely involve surface adatoms and related processes in their, "more macroscopic", description of plasma–surface interactions. This contribution sheds some light on these issues, introduces the basic approach to surface processes on plasma exposed surfaces, highlights unique features of the plasma environment that can be used to control these processes, and discusses some of the emerging challenges of this multidisciplinary field from the viewpoint of an applied plasma scientist.

This article is structured as follows. In Section 2, we describe the environment, spatial scales involved and the basic approach to assemble low-dimensional nanostructures such as crystalline quantum dots on solid surfaces exposed to the plasma. In the Section 3, the main details of a suitable plasma facility are presented. In Section 4, we discuss various plasma-related effects on the growth of nanoislanded nanocrystalline SiC films and Ge quantum dots (QDs) on Si(100) surfaces. In particular, we focus on the issues of growth rates, crystallinity, size and uniformity control, QD self-ordering, and also discuss how a plasma environment can modify the seemingly "unavoidable" Stranski–Krastanov mode of QD growth in moderately lattice-mismatched systems such as Ge/Si. The article concludes with the summary of the main challenges and the outlook for the future research in the field.

2. Bridging the 3D world of plasma physics and 2D world of surface science

Let us now consider the environment where the elementary self-organization processes occur. Fig. 1 shows a solid surface (denoted as a substrate) exposed to a low-temperature plasma. The size of the plasma bulk is of the order of fractions of a meter, which is a typical size of plasma processing reactors. The plasma bulk is separated from the solid surface by an area of uncompensated surface charge called a plasma sheath with a typical width ranging from microns to millimeters [6]. The electric field in the sheath accelerates positively charged ions towards the surface as shown in Fig. 1. Surface processes involve a few of the topmost atomic layers as well as adatoms migrating about the surface. As a result of assembly of these adatoms, nanostructures of a reasonably small number of atoms are formed. Thus, the spatial scales of the processes involved differ by up to 9 or even 10 orders of magnitude [4].

The above nanostructures in most cases emerge as nanoislands with size and shape determined by prevailing surface conditions such as energies of activation of adatom diffusion ε_a and desorption/re-evaporation to the gas phase ε_{evap}, chemical potential

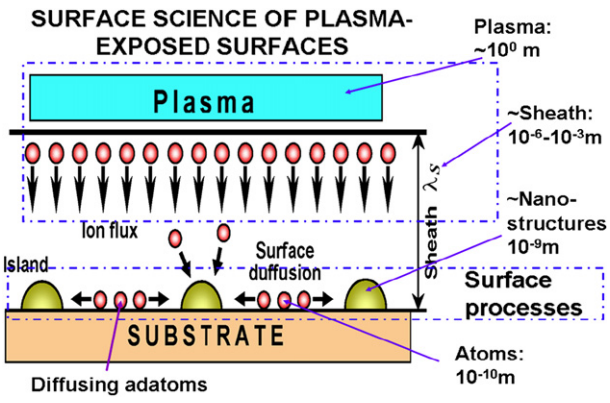

Fig. 1. A typical environment, basic processes, and spatial scales of the surface science of plasma exposed surfaces.

of the surface, distribution of surface stress, as well as available surface features such as stepped monoatomic terraces, dislocations, and surface defects [1]. The surface processes encircled by a dash-dotted line in Fig. 1 also involve small nanostructures being created since their presence substantially affects the distribution, motion, and self-arrangements of adatoms on the surface [7]. The line also encircles a few topmost atomic layers since interactions of adatoms with them determine the ability of adatoms to move and self-assemble. On the other hand, interaction of the nanostructures with the substrate atoms underneath determines the nanostructure growth processes and also sets a two-dimensional distribution of surface stress, which in turn affects adatom migration and assembly into nanostructures. In fact, this can already be considered as a simple self-organization process where the nanostructure growth affects the topmost atomic layers in the solid and the resulting stress affects surface adatom diffusion and evaporation, which in turn affects the nanoassembly process.

The above picture of self-organization is common to "mild" nanoassembly environments such as those in thermal Chemical Vapor Deposition (CVD) systems. What about the plasma environment of our interest here? What changes to this common scenario can we expect? Before we move on with this discussion, it is instructive to stress that present-day nanotechnology aims at achieving a *deterministic* (highly controllable and predictable) level in the synthesis of nanostructures and their assemblies. One of the main requirements to achieve the deterministic nanoscale synthesis of delicate nanoscale assemblies is to identify the most appropriate building units (BUs) [5] and properly balance the demand and supply of them. For example, if a square centimeter array of 10^{10} 1 nm-sized, crystalline, cubic silicon quantum dots is to be grown in a 1 s-long process, a minimum of approximately 3×10^{11} atoms would need to be delivered within 1 s. The required growth flux is thus $\Psi_{growth} = 3 \times 10^{11}$ atoms/cm^2 s. However, this amount should be increased to account for those adatoms that are unable to attach to the surface or desorb/evaporate shortly after adsorption. These processes may take a substantial fraction $\zeta (0 < \zeta < 1)$ of adatoms, especially at higher temperatures. Realistically assuming $\zeta = 0.5$, we obtain that the flux of adatoms lost form the surface Ψ_{loss} is also 3×10^{11} atoms/cm^2 s. Thus, the total incoming flux

$$\Psi_{tot} = \Psi_{growth} + \Psi_{loss} \quad (1)$$

under conditions of perfect match of BU balance and supply is 6×10^{11} atoms/cm^2 s, where Ψ_{tot} is the total incoming flux, Ψ_{growth} is the flux required for the growth, and Ψ_{loss} is the total loss flux. Taken that 1 cm^2 of silicon surface contains approximately 5×10^{14} (1 ML) silicon atoms, the "deterministically" required total incoming flux will be of the order of 10^{-3} ML/s. In real experiments, the total flux can differ from $\Psi_{growth} + \Psi_{loss}$. If $\Psi_{tot} < \Psi_{growth} + \Psi_{loss}$, the nanostructures would not grow or underdevelop during the adatom lifetime on the surface. On the other hand, if $\Psi_{tot} > \Psi_{growth} + \Psi_{loss}$, excessive delivery of building material results in a growth of undesired formations such as shapeless islands or amorphous films instead of the expected crystalline quantum dots.

The latter situation is quite common to plasma processing tools of applied plasma science. To show this, let us now estimate the flux of SiH_3 radicals from a typical silane-based plasma [8]. Assuming the radical density $n_r \sim 4 \times 10^{13}$ cm^{-3} and their thermal velocity $V_{Tr} \sim 500$ m/s, we obtain $\Psi_{tot} = (1/4) n_r V_{Tr} \sim 5 \times 10^{17}$ radicals/cm^{2}s, which is approximately 10^3 ML/s, which is in 6 orders of magnitude higher than required! This enormous oversupply of building units (although certainly good for the growth of bulk films, a traditional area of applied plasma science) is one of the main reasons why plasma tools have not been particularly successful in the synthesis of very delicate nanostructures such as quantum dots. This is in