

Supporting Information

Nano-herding: plasma-chemical synthesis and electric-charge-driven self-organization of SiO₂ nanodots

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1. High-resolution AFM measurements

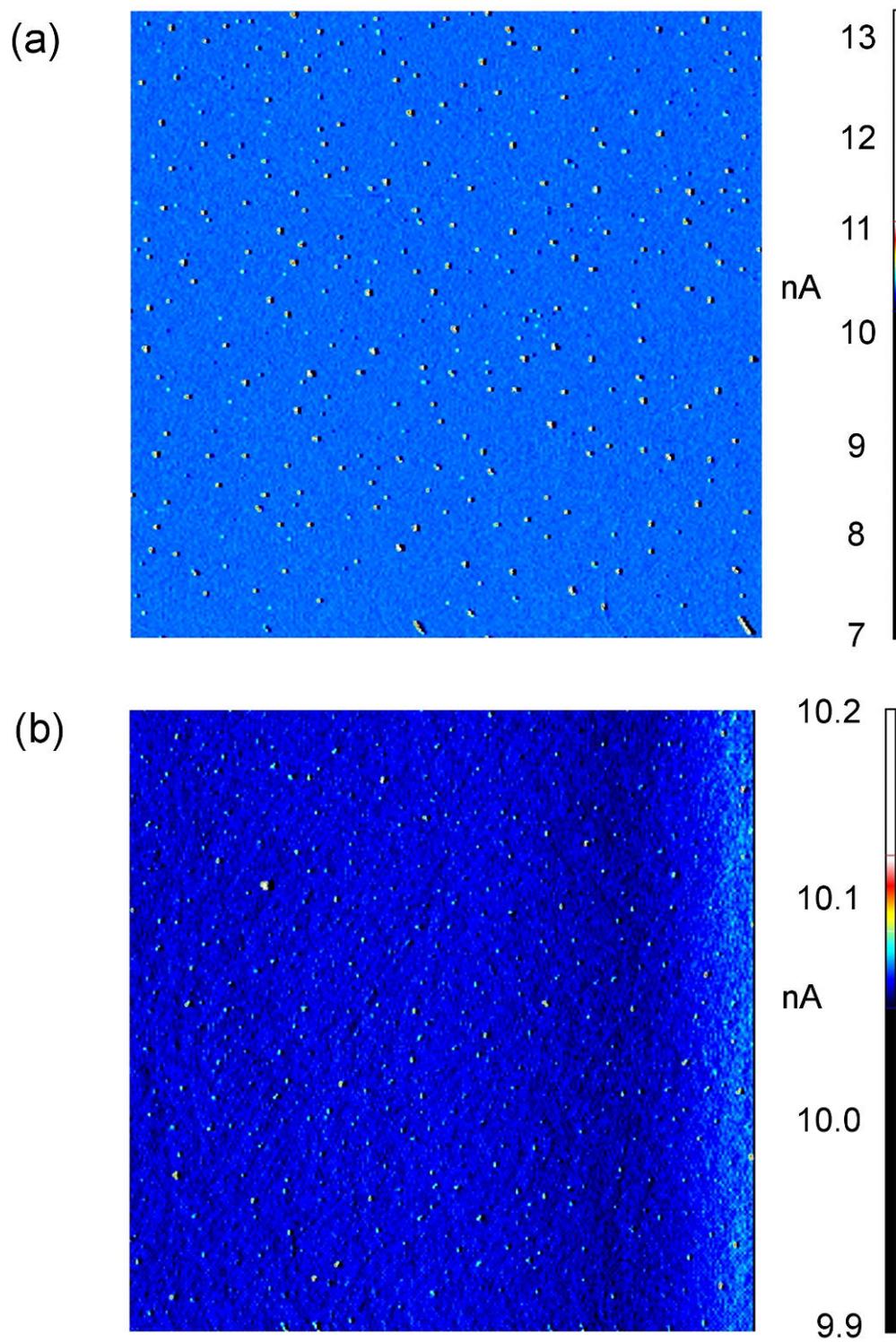


Figure S1. Nanodots on Si(111). 5 s (a) and 25 s (b) into the process.

2. Schematic of the Nanodot Array Formation

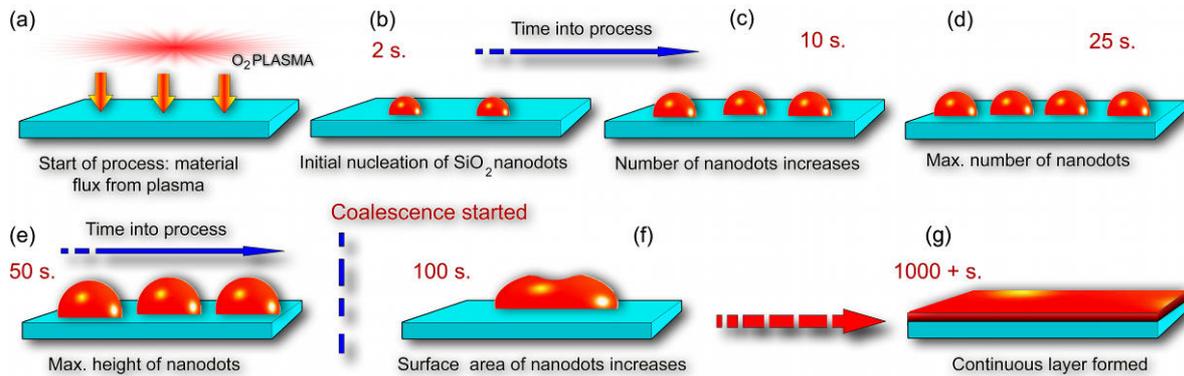


Figure S2. Schematics of the main stages of the process. Initial nucleation of nanodots (a,b); increase of nanodot number (c); max. number (surface density) of nanodots achieved in 25 s. into the process (d); increase of nanodot heights (e); increase of nanodot surface area (f), and eventually formation of the continuous layer (g).

3. Details of the Model and Simulations

When simulating the kinetics of the nanodot array formation and growth of the nanodots, the main problem is to simulate the fluxes of adsorbed atoms (silicon and oxygen) to the borders of nucleated nanodots (we assumed that the nanodots nucleate on the nano-hillocks on the clean silicon surface). To calculate the diffusion flux of adatoms to the nanodot border we used a vector of surface diffusion activation energies $\mathfrak{S}(\varepsilon_1, \varepsilon_2, \varepsilon_k)$ associated with various features present on the surface. Here, ε_i is the diffusion activation energy of the atom adsorbed on an i -th surface feature. In these simulations, we have taken into account the following surface features: regular (defect-free) crystalline lattice, surface vacancies, interstitial atoms on the surface, dislocations, step terraces, and nano-grain boundaries. The \mathfrak{S} vector depends on the densities of each feature η_i . Experimental values of the diffusion activation on various surface defects are not currently available, so we have used the approximate values of the

energies obtained by considering a nature of each specific surface defect. For example, the diffusion activation on a surface vacancy was estimated by assuming that the energy of a Si atom detachment from the vacancy is 1.3 times higher than the detachment from the defect-free surface.¹ The adatom activation energy at a step terrace was approximated as a doubled activation energy for the defect-free surface; the activation energy on a nanodot boundary was assumed to be equal to the activation energy at a step terrace, etc. The densities of the surface defects were taken from the characteristics of the experimental substrates.²

The simulations were based on the equation for the adatom surface density $\dot{n} = D\Delta(n) + \Psi_{\Sigma}$, where Δ is the Laplace operator, n denotes the density of adatoms on Si surface, and Ψ_{Σ} is the effective atom flux to the substrate (influx from the plasma minus the flux of evaporation/detachment from the substrate surface):

$$\Psi_{\Sigma} = S_s \Psi_o - (S/\lambda^2) \nu_0 \exp(\varepsilon_s/kT_s), \quad (1)$$

where S is the area of the substrate surface, Ψ_o is the flux of oxygen atoms and ions from the plasma to the surface, k is the Boltzmann's constant, T_s is the surface temperature, ν_0 is the frequency of lattice atom oscillations, λ is the lattice constant, and ε_s is the energy of atom evaporation from the substrate surface.

The flux of the diffusing adsorbed atoms to the border of the individual nanodot is:

$$\Psi_{s.i} = -l \frac{m}{\lambda^3 \rho} \left[D \frac{\partial n}{\partial x} \right], \quad (2)$$

where m , ρ_m , and l are the adatom mass, silicon oxide density, and perimeter of the nanodot, accordingly. The effective surface diffusion coefficient D can then be obtained in the form

$$D = \lambda^2 \nu_0 \exp(-\bar{\varepsilon}_d/kT_s), \quad (3)$$

where the effective surface diffusion activation energy, $\bar{\varepsilon}_d$, is calculated using the vectors \mathfrak{S} and the vector of densities of each feature, \mathbf{N} :

$$\bar{\varepsilon}_d = \frac{\Re \cdot \mathbf{N}}{\Theta \cdot \mathbf{N}} = \frac{\sum \varepsilon_k \eta_k}{\sum \eta_k}, \quad (4)$$

where Θ is a unit vector.

To solve the equation for the adatom surface density, we used a simulated electric field to estimate the change in the surface diffusion activation energy due to the adatom interaction with the electric field, taking into account the polarizability α of adatoms. In this case, the total dipole moment in the electric field $E(r)$ is $\tilde{P} = \tilde{p} + \alpha E$, where \tilde{p} is the dipole moment of an adatom. Thus, the energy acquired by an adatom in one jump along the lattice spacing λ_a is:

$$W_e = \frac{\partial E}{\partial r} (\tilde{p} + \alpha E(r)) \lambda_a. \quad (5)$$

In this case, the electric field-modified effective diffusion activation energy reads

$$\bar{\varepsilon}_{de} = \bar{\varepsilon}_d + W_e / kT_s. \quad (6)$$

Hence, the calculation of the electric field-dependent $\bar{\varepsilon}_{de}$ is reduced to the determination of the microscopic electric field topography. In the vicinity of the surface with a nanodot, the electric field is described by the Poisson equation $\Delta\varphi = \rho_e/\varepsilon_0$, where ρ_e is the density of electric charges in the plasma-surface sheath, in the vicinity of the substrate surface. The electric field near small particles is very strong due to the very large surface curvature. This is why the density of electric charges in the plasma-surface sheath can be neglected, and the electric field can be found from the Laplace equation $\Delta\varphi = 0$, where φ is the electric potential.

More details on the model can be found in our previous publications.^{3,4}

4. Electron and Ion Fluxes to the Substrate Immersed in Plasma

In the low-temperature non-equilibrium plasma (with the electron energy reaching 10 eV and ion temperature of about 300 K), the electron fluxes from plasma to the substrate surface are very strong. When the substrate surface is under ‘floating’ potential, the electron flux to the surface is equal to the ion flux, and these fluxes can be estimated as $\varphi = V_B \times n_{i,e}$, where $V_B = \sqrt{2\varepsilon_e/m_i}$ is the Bohm velocity, $n_{i,e}$ is the ion/electron density in plasma, ε_e is the electron energy and m_i is the ion mass.⁵ With the typical electron energy of 10 eV and ion/electron density $2 \times 10^{16} \text{ m}^{-3}$ in the radio-frequency low-temperature plasma, the ion and electron fluxes can reach $10^{20} \text{ m}^{-2}\text{s}^{-1}$. These strong fluxes ensure material supply to the surface, and simultaneously, they sustain a negative floating potential which in turn causes electric-field self-organization in the nanodot ensemble.

5. Schematic of the experimental setup

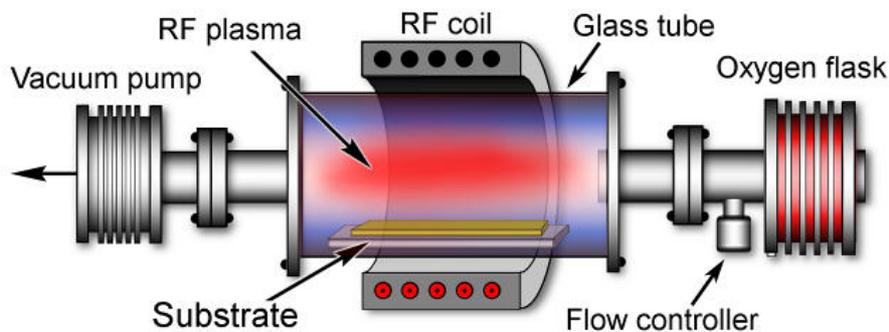


Figure S3. Schematic of the experimental setup used to grow arrays of SiO₂ nanodot arrays.

References

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