Combinatorial Masked Deposition:

Simple Method to Control Deposition Flux and Its Spatial Distribution

Suguru Noda*, Yuya Kajikawa, and Hiroshi Komiyama

*Correspondence:

Dr. Suguru Noda

Department of Chemical System Engineering, School of Engineering,

The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Fax: +81-3-5841-7332

Phone: +81-3-5841-7330

E-mail: noda@chemsys.t.u-tokyo.ac.jp

Abstract

Deposition flux is an important factor that determines the structures of vapor-deposited materials. However, controlling this flux over a wide range is difficult using only a single apparatus. In this work, we developed a simple method, called *combinatorial masked deposition* (CMD), that enables a series of deposition fluxes and their respective distribution to be realized on a single sample by just setting a mask with holes of different sizes above a substrate. The degree of reduction in deposition flux can be controlled by the hole size and distance between the given point and the hole. The characteristics and applicability of CMD were evaluated by two experiments. In the first experiment, Cu nanoparticles were formed by sputter-deposition on a-SiO_2 at different Cu deposition fluxes. The nanoparticles had a higher number density and smaller size when deposited at 0.80 nm/s for 2.5 s than when deposited at 0.014 nm/s for 140 s. In the second experiment, metal-induced crystallization of a-Si was done with spatially distributed Ni additives. The CMD method can realize a series of Ni flux distributions and was successfully used to form 100 different profiles of Ni concentration on a single sample, thus enabling efficient screening of concentration profiles to enhance grain size.

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1. Introduction

The combinatorial approach is a key concept in improving the productivity of experimental investigations. In the materials research field, this concept has been extensively used, focusing mainly on the relationship between the composition and properties of the material [1]. The relationships among process, structure, function, and application of materials are crucial for materials technology. The focus in those above-mentioned combinatorial studies in the materials research field has been the “structure-function” relationship. In contrast, the “process-structure” relationship has not been extensively studied using the combinatorial approach. Here, we developed a simple combinatorial approach to this process-structure relationship.

The effect of deposition flux on island structure is an example of the process-structure relationship. Island nucleation and growth processes have received considerable attention due to both fundamental interests and technological importance, and thus have been extensively studied both experimentally and theoretically, as well reviewed in Refs. 2 and 3. Figure 1 schematically shows island nucleation and growth processes occurring on a substrate surface. In the theoretical studies, deposition, diffusion, and aggregation of incoming species are considered as elementary processes, yielding models called *DDA models*. Analytical approaches based on a mean field approximation [4] or on kinetic Monte Carlo simulations [2, 3] are used to predict the structure of materials, such as island number density and island size distribution. The maximum number density of islands, N_{max}, is a major concern in materials technology because it is not only a good index of structure of particle arrays but also affects the properties of such arrays. The DDA models have yielded the general relation, $N_{max} \sim (F/D)^{\chi}$, where F is the deposition flux, D is the surface diffusion coefficient, and χ is a constant that reflects other elementary processes shown in Fig. 1, such as adsorbate desorption, trapping of the adsorbates by surface defects, attachment and detachment of adsorbate from islands, island deformation, and size-dependent island migration and coalescence [2- 4]. In DDA models, the rate of elementary processes is usually normalized by the average atomic distance and the vibrational frequency of the condensed phase. The modeling results have been compared with experimental results obtained, for example, by molecular beam epitaxy (MBE), evaporation, and cluster beam deposition [2, 3]. Compared with these methods, sputter-deposition is more commonly used in practical applications and has advantages of relatively high deposition flux and applicability to most materials. But the deposition flux can typically be controlled within the range of only one order of magnitude when a single sputtering apparatus is used, which is not wide enough for comparison with modeling. Therefore, a simple method to control deposition flux by several orders of magnitude is needed for systematic investigations of the structural evolution under different deposition fluxes.

The effect of the spatial distribution of additive concentrations in amorphous materials on their crystallization behavior is another example of the process-structure relationship. Synthesizing polycrystalline silicon thin films with large grain sizes on glass substrate is important for the application of thin film transistors and solar cells. In solid-phase crystallization of amorphous Si (a-Si) by thermal annealing, the grain size of crystal Si (c-Si) is typically in the sub micrometer range or less due to its relative high nucleation rate compared with its low growth rate, and the annealing temperature is relatively high (typically about 950 K or above). Addition of metal significantly changes the crystallization behavior by so-called *metal-induced crystallization* (MIC). Ni is known to have significant effect; for example, Ni reacts with a-Si to form $NiSi_X$, and once a-Si/ $NiSi_2$/ c-Si interface is formed, $NiSi_2$ moves toward a-Si, thus leaving c-Si epitaxially [5] as shown in Fig. 2a. This *metal-induced lateral crystallization* (MILC) sometimes yields c-Si with grain size of about 50 μm [7]. Many studies have been done on adjusting Ni patterns to increase the MILC length, which is the distance between the edge of a Ni pattern to the crystal growth front [7, 8]. If one dimensional (1D) line patterns of Ni are formed on a-Si, $NiSi_2$ crystallites forms on the lines at a high number density. $NiSi_2$ crystallites then move toward a-Si regions, thus forming elongated grains of c-Si (Fig. 2b). Therefore, by using 1D line patterns, large grain sizes are not expected. If zero dimensional (0D) dot patterns of Ni are used, a small number of $NiSi_2$ crystallites forms at the dots. $NiSi_2$ crystallites then move toward a-Si regions radially from each dot, and thus the grains of c-Si grow large in two dimensions (2D) (Fig. 2c). The length of the a-Si/ $NiSi_2$/ c-Si interface, however, increases as MILC proceeds, and therefore the thickness of the $NiSi_2$ layer decreases and MILC stops [7, 9]. Our proposal is to use radial concentration profiles of Ni additives, which might be a breakthrough in increasing the MILC length. Continuous supply of Ni to the a-Si/ $NiSi_2$/ c-Si interface might continue MILC and yield large grains of c-Si (Fig. 2d). A simple method to realize a series of concentration profiles is needed to systematically and efficiently investigate their effects on MILC and to find a proper profile that yields large grain size.

Collimated sputtering is one method to control the deposition flux. To realize conformal deposition in trenches and via holes that have large aspect ratios in ultra-large-scale integrated (ULSI) devices, the angle distribution of incoming species is narrowed by placing a physical filter between the sputtering cathode and the substrate [10]. As a consequence, deposition fluxes are significantly reduced, which is a major drawback against using collimated sputtering in practical applications.

Our proposal is a simple method to utilize this decrease in deposition flux for systematic experimental investigations of the process-structure relationship. In this method, by setting a mask with holes of different sizes just above a substrate, both the maximum deposition flux and the spatial distribution for each hole can be systematically controlled. We call this simple method, *combinatorial masked deposition*, or CMD. The concept of systematic and efficient screening of experimental conditions (deposition flux and distribution) by using the CMD method is similar to other combinatorial approaches where systematic and efficient screening is realized by using libraries prepared by a combination of elements. By using the CMD method, we carried out preliminary experimental investigations of two systems. One system was the Cu nanoparticle formation on a-SiO_2 substrates by sputter-deposition to evaluate the effect of deposition flux on the size and number density of Cu nanoparticles. The second was Ni-MIC of a-Si, in which radial concentration profiles of Ni additives were formed on a-Si substrate by using the CMD method to enhance MILC length.

2. CMD method

Figure 3 shows a schematic of CMD method applied to a sputter-deposition system. Differently from collimated sputtering, a mask with holes is set just above a substrate as shown in Fig. 3a. The CMD method can be effective when the following three conditions are satisfied: (i) mask-source distance >> mean free path of the deposition species, (ii) mask-substrate distance << mean free path of the deposition species, and (iii) sticking probability ~ 1. Under these conditions, the flying direction of the deposition species is randomized by sufficient gas-phase collisions in the space between the source and the mask and therefore the species passes through the holes at randomized injection angles (i), the flux of the species is diluted as the species flies straightly away from the holes with negligible gas-phase collisions in the space between the mask and the substrate (ii), and then the species stick at the target point on the substrate without being reflected at the substrate surface (iii). The degree of reduction in deposition flux is then simply determined by the solid angle of the hole from the target point on the substrate. If the condition (ii) is not satisfied, gas-phase collisions make the deposition species rather diffusion controlled and this make it difficult to predict the degree of reduction in deposition flux. If the above-mentioned three conditions are satisfied, the CMD method can also be applied to deposition methods other than sputter-deposition.

In the two preliminary experiments using the CMD method as explained in Sections 3 and 4, the masks were Si. Patterns for a hole array were made on (100) Si wafers by photolithography and then the wafers were wet-etched by hydrazine. Due to the negligibly small etching rate of {111} planes compared to the other planes, quadrangular pyramids were formed as schematically shown in Fig. 3b. The degree of reduction in the flux of the deposition species can be expressed by:

$$\frac{F(X,Y,0)}{F_0} = \frac{1}{2\pi}\int_{x_{\min}}^{x_{\max}}\int_{y_{\min}}^{y_{\max}} z_0 \left\{(x-X)^2 + (y-Y)^2 + z_0{}^2\right\}^{-\frac{3}{2}} dxdy \qquad (1)$$

where (x, y, z) is the coordinate shown in Fig. 3b, $F(X, Y, 0)$ is the incoming flux at the position (X, Y, 0) on the substrate, F_0 is the incoming flux without a mask, and ($x_{\min}$, $y_{\min}$, z_0), ($x_{\max}$, $y_{\min}$, z_0), ($x_{\min}$, $y_{\max}$, z_0), and ($x_{\max}$, $y_{\max}$, z_0) are the corners of the upside-down quadrangular pyramid where the deposition species pass through to the substrate. By numerical integration, the reduction ratio of the incoming flux can be calculated for each target point (X, Y, 0) and then used to calculate the spatial distribution of the incoming flux for each hole.

Figure 4 shows representative calculated spatial distributions for two hole sizes, h = 1.0 and 0.050 mm, and wafer thickness t = 0.32 mm and mask-substrate distance (gap) g = 1.0 mm. The figure reveals that both the maximum deposition flux, $F_{\max}$, and the spatial distribution limit, σ, can be significantly affected by the hole size. The effect of the deposition flux can be investigated by placing smaller substrates than σ, such as grids for transmission electron microscopy (TEM), just below each hole within the central region with uniform deposition flux, and the effect of the spatial distribution of deposition flux can be investigated by placing larger substrates than σ.

3. Flux control: application to the study of island nucleation and growth in sputter-deposition.

The CMD method was applied to study the effect of deposition flux on the structure of Cu nanoparticles on a-SiO_2 formed by sputter-deposition. Figure 5 schematically explains an example of the design of experimental conditions to investigate the effect of deposition flux on the structure of deposits. By setting a mask with N holes of different sizes parallel to the substrate, N samples of different deposition amount with different flux can be prepared in a single experimental run. By carrying out ~2N runs of different deposition times, ~ N^2 samples can be obtained, which can then be used both for the comparison of the deposit structure of the same deposition amount formed by different deposition fluxes and for the investigation of the structural evolution of the deposits with increasing deposition amount. In this example, the CMD method can reduce the experimental runs for deposition by a factor of about N.

Figure 6 shows transmission electron microscopy (TEM) images of Cu nanoparticles sputter-deposited on TEM grids capped with a-SiO_2 at two different deposition fluxes. Deposition thickness was kept at 2 nm, which was estimated from the growth rate of continuous films multiplied by the deposition time. Cu nanoparticles clearly had different structures for different deposition flux. For the higher (Fig. 6a) and lower deposition flux (Fig. 6b), the volume-based average projected area diameter was 3.5 and 5.8 nm, respectively, and the island number density was 1.9×10^{16} and 0.69×10^{16} /m^2, respectively.

These preliminary results show the effectiveness of CMD in systematically studying the effect of deposition flux. To realize the quantitative comparison between theory and experiments, which is very important, systematic experimental results are indispensable. By carrying out experiments under the conditions of Fig. 5, a time profile of number density of islands, for example, can be obtained for each deposition flux. Then N_{max} can be determined and the relation between N_{max} and F can be derived. By reaching this stage, the quantitative comparison between the experimental result with the theoretical one, i.e. $N_{max} \sim (F/D)^{\chi}$, becomes possible. Further works are currently ongoing to achieve this goal by the aid of CMD, which enables efficient experiments under numerous conditions.

4. Distribution control: application to the study of Ni-MILC of a-Si

As mentioned in the Introduction, Ni-MILC of a-Si with proper Ni concentration profiles might be a breakthrough to achieve large-grained c-Si films. Here, CMD was applied to form Ni concentration profiles on an a-Si layer. In the profile formed under each hole, Ni concentration was the highest at the center, i.e. just below the hole, and decreased as the distance from the center increased (Figs. 4a, b). During thermal annealing, crystalline nucleation will start at the center, then the a-Si/ $NiSi_2$/ c-Si interface will move radially toward surrounding regions with lower Ni concentration, and finally, sectoral grains of c-Si will form. During the radial movement of the a-Si/ $NiSi_2$/ c-Si interface, the length of $NiSi_2$ continuously increases and Ni concentration profile enables a continuous supply of Ni to $NiSi_2$. For the ideal Ni concentration profile to achieve a constant thickness of $NiSi_2$, Ni concentration should be inversely proportional to the distance from the center of the profile. The Ni concentration profile formed by the CMD method is similar but not exactly the same as the ideal profile. Therefore, to determine the appropriate Ni concentration profile to enhance MILC, numerous patterns with different maximum Ni concentrations and spatial distribution limits were systematically examined here by using the CMD method.

Figure 7 schematically shows an example of the mask layout to produce a series of spatial distributions of deposit on a single substrate. The deposition amount passing through a single hole can be changed by simply changing the hole size, and the area where deposition occurs can be changed by simply changing the mask-substrate gap. The mask-substrate gap can be easily changed by tilting the mask on the substrate. If one array of N holes is prepared for one hole size and N arrays are prepared for N different hole sizes, then N^2 patterns can be realized on a single substrate in a single deposition run. In this example, the CMD method can reduce the number of required experimental runs for deposition by a factor of N^2.

Figure 8 shows optical microscopy images of a crystallized a-Si sample with 100 Ni patterns formed by using the CMD method. Each circle represents a single Ni pattern. The sample structure was 100 Ni patterns on a sputter-deposited 100-nm-thick a-Si layer on a alumino-silicate glass substrate. The Ni thickness was set at 7.5 nm without the mask, and Ni thickness on the patterns was reduced according to Eq. (1). Annealing was performed at 773 K for 90 h under vacuum. This figure reveals that a bright, white region appeared in the central part of each pattern, surrounded by a bright, brown region (gray in Fig. 8). micro-Ramann scattering spectroscopy showed that the central bright regions were composed of crystalline Si, whereas the surrounding brown regions were composed of a-Si, suggesting that the Si crystallization started from the central region where Ni existed with higher concentration than in the surrounding region. Although an irregularly large patterns caused by an irregularly large hole in the mask is evident as indicated by an arrow in the figure, in general the patterns increased in area as g and h increased and the boundaries between crystalline Si and a-Si became less distinct as g increased. Further study is currently ongoing to investigate the relation between the Ni-MIC process and the Ni concentration profiles.

By applying the CMD method, 100 Ni patterns were examined in a single sample. The result shown in Fig. 8 required only 5 hours, including sample preparation and optical microscopy observation, but not the time for annealing during which the samples are just left in the furnace (90 h in this case). After screening the Ni-MIC conditions by this method, detailed investigations using TEM, for example, can be done just for important patterns out of the 100 possible. Thus, the CMD method will enable efficient screening of Ni-MIC conditions.

5. Conclusions

An experimental method, called *combinatorial masked deposition* or CMD, was developed that enables a series of deposition fluxes and their respective distributions in a single sample by just setting a mask with holes of different sizes above a substrate. The characteristics and applicability of CMD were evaluated by two experiments. In the first experiment, the effect of the deposition flux on the structure of Cu nanoparticles formed by sputter-deposition of Cu on a-SiO_2 was examined. The nanoparticles had a higher number density and smaller size when deposited at higher deposition rate but keeping the deposition amount unchanged. In the second experiment, Ni was deposited on a-Si layer with radial Ni concentration profiles by utilizing the spatial distribution of deposition flux in CMD, and the effect of the Ni concentration profiles on Ni-MIC process was examined. The CMD method was thus successfully used to form 100 different profiles of Ni concentration on a single sample, clearly demonstrating that CMD enables efficient screening of conditions of Ni-induced crystallization.

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References

[1] X.-D. Xiang, X. Sun, G. Briceno, Y. Lou, K.-A. Wang, H. Chang, W. G. Wallace-Freedman, S.-W. Chen, P. G. Schultz, Science, 268 (1995) 1738.

[2] H. Brune, Surf. Sci. Rep. 31 (1998) 121.

[3] P. Jensen, Rev. Mod. Phys. 71 (1999) 1695.

[4] J. A. Venables, G. D. T. Spiller, M. Hanbucken, Rep. Prog. Phys. 47 (1984) 399.

[5] C. Hayzelden, J. L. Batstone, J. Appl. Phys. 73 (1993) 8279.

[6] S. W. Lee, S. K. Joo, IEEE Electron Device Lett. 17, (1996) 160.

[7] Z. Jin, K. Moulding, H. S. Kwok, M. Wong, IEEE Trans. Electron. Devices 46 (1999) 78.

[8] C. Y. Yuen, M. C. Poon, W. Y. Chan, M. Qin, J. Appl. Phys. 92 (2002) 6291.

[9] A.R. Joshi, T. Krishnamohan, K. C. Saraswat, J. Appl. Phys. 93 (2003) 175.

[10] S. M. Rossnagel, D. Mikalsen, H. Kinoshita, J. J. Cuomo, J. Vac. Sci. Technol. A 9 (1991) 261.

Figure Captions

Figure 1. Schematic of nucleation and growth processes of nanoparticles on a substrate surface.

Figure 2. (a) Cross-sectional images of the phenomena occurring during Ni-MIC. Top view of the resulting structures after Ni-MIC with a (b) line pattern of Ni and (b) dot pattern of Ni. (d) A radial profile of Ni concentration applied to Ni-MIC, which might enhance MILC.

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Figure 4. Spatial distributions of deposition flux calculated for t = 0.32 mm, g = 1.0 mm, and h = (a) 1.0 and (b) 0.050 mm.

Figure 5. Example of the design of experimental conditions to investigate the effect of deposition flux on the structure of deposits at nucleation and growth stages. Open circles represent the conditions realized by the CMD method which are suited for the investigation of nucleation and growth stage, and the open circles connected by a line represent the conditions achieved in one deposition run for a given deposition time. Bar shows the flux realized by a single sputter-deposition apparatus without the CMD method.

Figure 6. TEM images of Cu nanoparticles formed by sputter-deposition of Cu on SiO_2 substrates at a (a) high deposition flux of 0.80 nm/s for 25 s and (b) low deposition flux of 0.014nm/s for 140 s.

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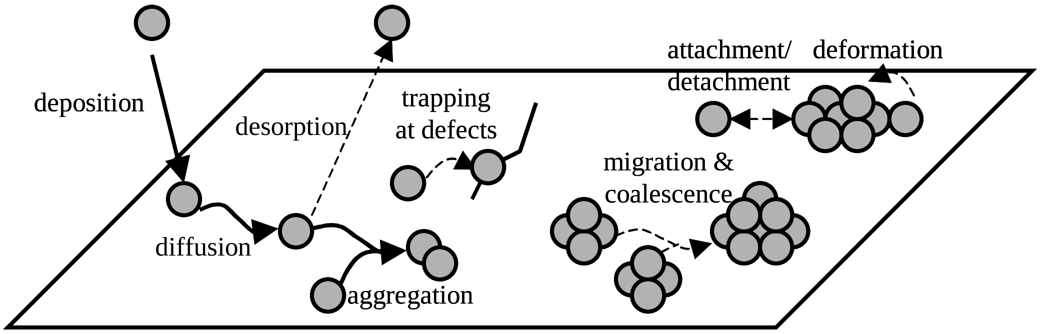

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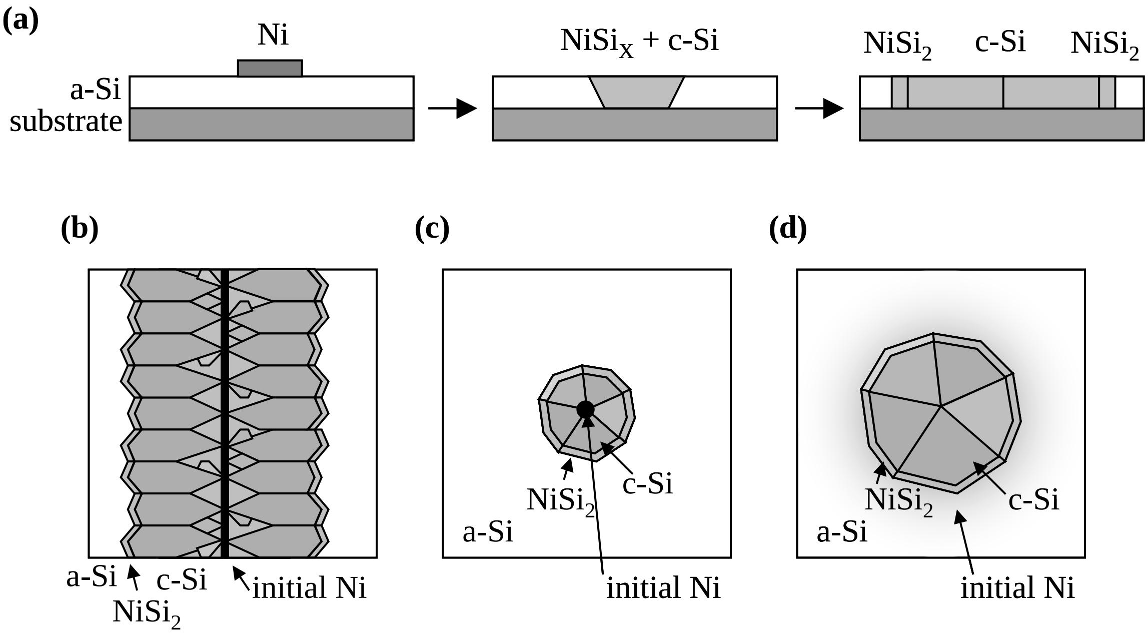

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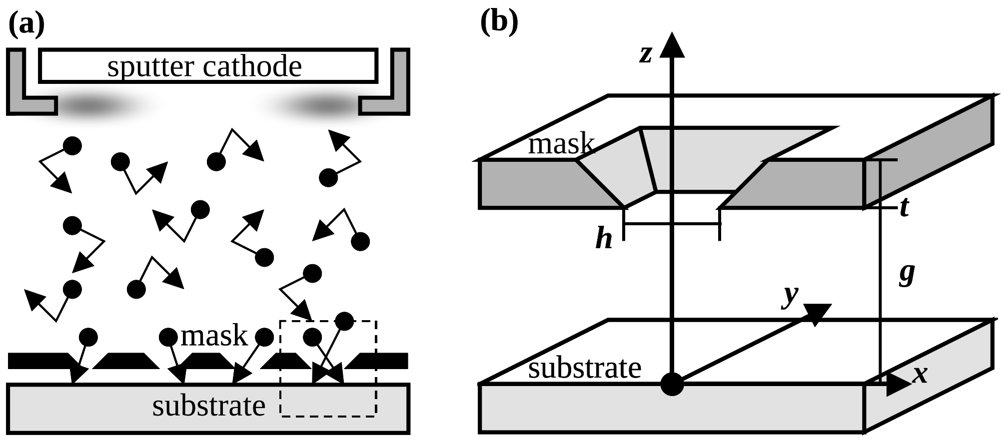

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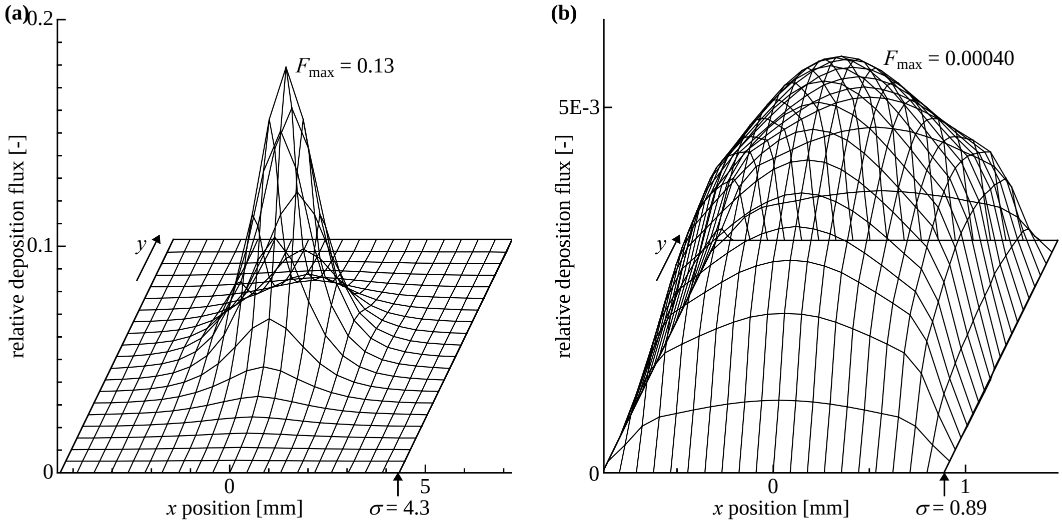

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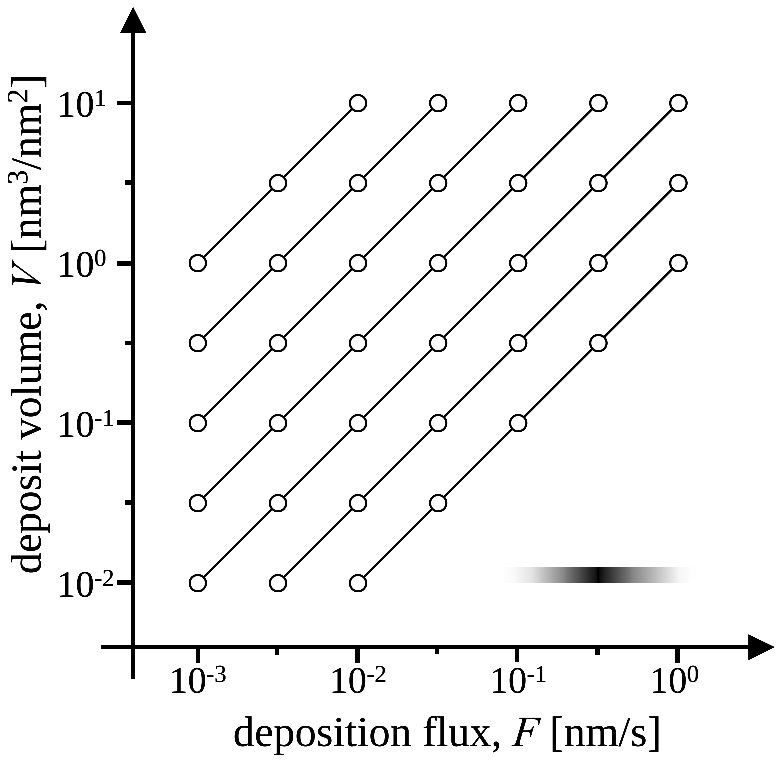

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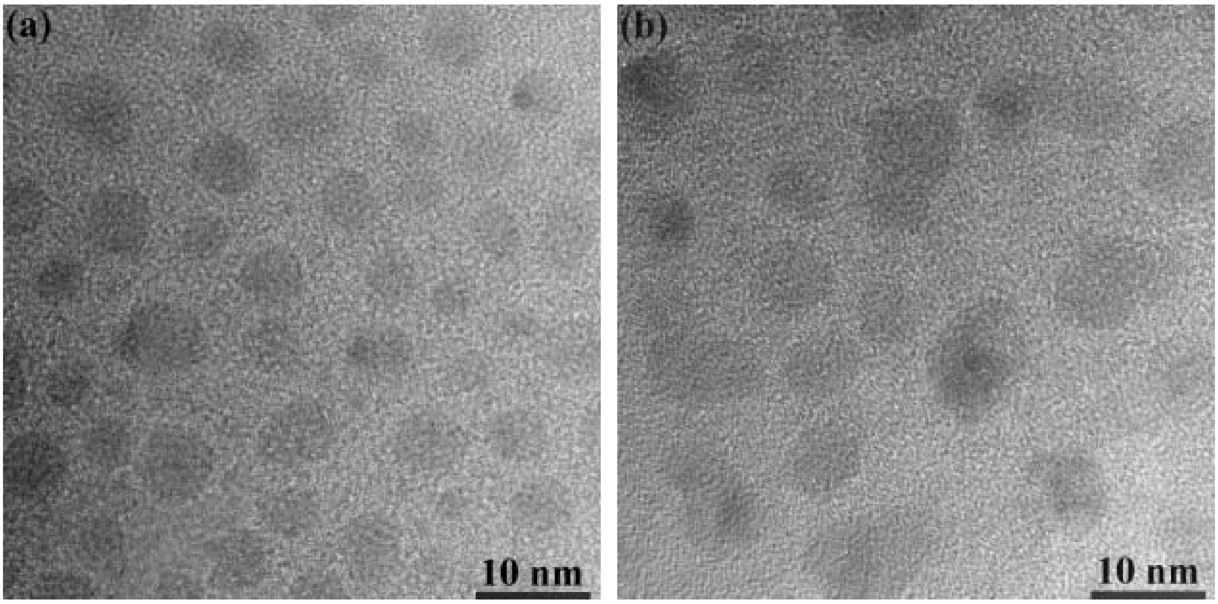

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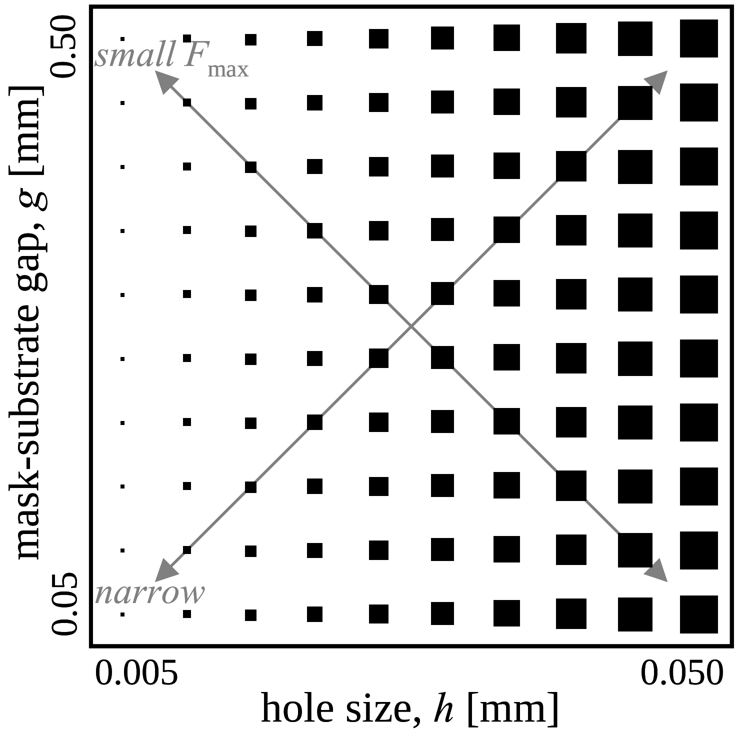

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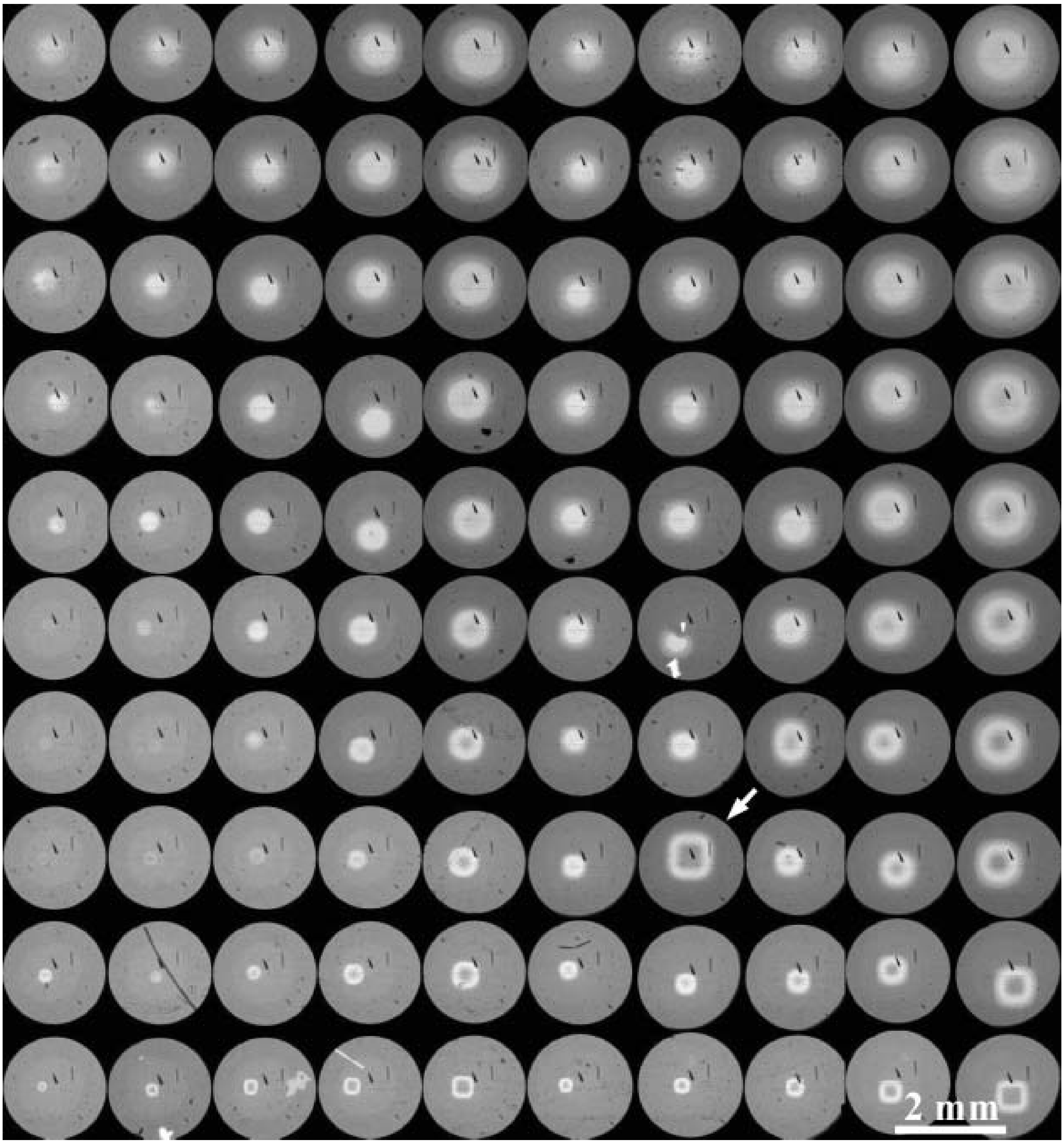

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