

Electron beam lithography using SiO₂ as a sensitive layer

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Abstract: In this paper, we study the capabilities and some features of direct electron-beam lithography using a layer of silicon dioxide SiO₂ (grown by thermal oxidation) as a resist sensitive to the action of the electron beam and a developing composition based on an aqueous solution of dilute buffered hydrofluoric acid. Additional factors influencing the lithography result (the existence of an initial period of exposure effect enhancement) are found. To explain this feature, a hypothesis about the mechanism of the influence of the electric charge introduced into the SiO₂ layer (during exposure) on the process of further development of the latent image is proposed. As a measure eliminating the manifestations of contamination phenomena, an approach using a sacrificial copper layer applied during the exposure period is proposed. A rationale for choosing the metal of the sacrificial layer is given based on experimental observations and a hypothesis about the possible chemical composition of contamination spots in the exposed areas. The parameters of the direct lithography process on SiO₂ known from the literature are clarified. The nonlinear nature of the effect of the electron beam on the silicon dioxide layer is found and simple empirical dependencies that allow a quantitative description of the result of the lithography process for the case of large-scale structures are proposed. It is shown that even when using a sacrificial copper layer, it is possible to achieve a lithographic process resolution of no worse than 30 nm.

Keywords: electron beam lithography; grayscale lithography; inorganic resists; contamination; charging effect.

For citation: Zubov DN, Sokolov SA, Eganova EM, Yakovlev VB. Electron beam lithography using SiO₂ as a sensitive layer. *Journal of Advanced Materials and Technologies*. 2025;10(2):129-140. DOI: 10.17277/jamt-2025-10-02-129-140

Электронно-лучевая литография с использованием SiO₂ в качестве чувствительного слоя

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Аннотация: Изучены возможности и некоторые особенности прямой электронно-лучевой литографии с использованием слоя диоксида кремния SiO₂ (выращенного термическим окислением) в качестве резиста, чувствительного к действию электронного луча, и проявляющего состава на основе водного раствора разбавленной буферизованной плавиковой кислоты. Найдены дополнительные факторы, влияющие на результат литографии (существование первоначального периода усиления эффекта экспонирования). Для объяснения данной особенности предложена гипотеза о механизме влияния внедренного в слой SiO₂ (в процессе экспонирования) электрического заряда на процесс дальнейшего проявления скрытого изображения. В качестве меры, устраняющей проявления контаминационных явлений, предложен подход с использованием жертвенного слоя меди, наносимого на период проведения экспозиции. Приведено обоснование выбора металла жертвенного слоя на основе экспериментальных наблюдений и гипотезы о возможном химическом составе контаминационных пятен в экспонированных областях. Уточнены известные из литературы параметры процесса прямой литографии на SiO₂. Найден нелинейный характер эффекта воздействия электронного луча на слой диоксида кремния,

и предложены простые эмпирические зависимости, позволяющие количественно описать результат процесса литографии для случая крупномасштабных структур. Показано, что даже при использовании жертвенного слоя меди возможно достижение разрешения литографического процесса не хуже 30 нм.

Ключевые слова: электронно-лучевая литография; полутонная литография; неорганические резисты; контаминация; эффект зарядки.

Для цитирования: Zubov DN, Sokolov SA, Eganova EM, Yakovlev VB. Electron beam lithography using SiO₂ as a sensitive layer. *Journal of Advanced Materials and Technologies*. 2025;10(2):129-140. DOI: 10.17277/jamt-2025-10-02-129-140

1. Introduction

Direct electron beam lithography on thermally grown silicon dioxide films has been known for a long time. The relevance of such studies is related, among other things, to the fact that silicon dioxide is often included in various micro- and nanodevices. However, most of such studies were conducted using high-energy electron beams [1–8]. An interesting feature of this process is high lithography resolution. The works [1, 5–7] describe the process of direct electron beam lithography on SiO₂ at an electron energy of 300 keV and show the achieved half-step resolution of 7.5 nm on a free SiO₂ membrane on Si₃N₄ [1] and 5.4 nm in the work [7] (also on a free membrane). The papers [3, 4, 8, 9] describe the application of direct lithography on SiO₂/Si/SiO₂ layers with exposure to electrons with an energy of 50 keV to create elements with sizes of less than 10 nm [3, 9]. In the paper [10], the process of direct electron beam lithography on SiO₂ was used to create structures of field-effect transistors based on silicon nanowires (electron energy during exposure is 30 keV). Among the papers in which the study of electron beam lithography was carried out using low-energy electrons (units of kiloelectron volts), the paper [11] can be mentioned. One of the discovered advantages of using electron beams with comparatively low energies is the higher sensitivity of SiO₂ to their impact. However, this paper did not evaluate the capabilities of direct lithography on SiO₂ in terms of resolution. The characteristics of electron beam lithography (and in particular the resolution) on SiO₂ films as a resist are of interest, since it is precisely for electron beams with comparatively low energies that an alternative mechanism for the formation of latent images can be proposed, potentially allowing for a significant increase in the dose sensitivity of the lithography process.

An alternative mechanism for the formation of latent images is the well-known phenomenon of charging dielectrics irradiated by an electron beam. This phenomenon is usually considered as a factor that interferes with the exposure process in electron-

beam lithography and in the study of samples in a scanning electron microscope. However, there are works that show the fundamental possibility of using this phenomenon to form microstructures [12, 13]. Thus, the paper [12] experimentally shows the effect of an electric field created in a SiO₂ layer (using quartz glass as an example) on the rate of its dissolution in hydrofluoric acid. Thus, the presence of a local electric charge in the SiO₂ dielectric layer (formed under the action of an electron beam) can lead to a change in the local etching rate of the dielectric film. This mechanism is of interest because the expected maximum dose sensitivity of the lithography process is much higher than that usually observed for SiO₂ films, and can be compared with the sensitivity of resists with the so-called chemical enhancement (i.e., on the order of units of $\mu\text{C}\cdot\text{cm}^{-2}$). This value can be estimated using a simple model of a flat capacitor. Of course, the estimate obtained on the basis of such a model will only be approximate. Thus, the paper [12] presents the characteristic electric field strength, at which the effect of changing the etching rate of SiO₂ is observed (the first hundreds of $\text{V}\cdot\mu\text{m}^{-1}$). Also, knowing the value of the dielectric constant of SiO₂, it is possible to calculate the specific charge density on the plates in the flat capacitor model using the known formula (1):

$$q = \frac{Q}{S} = \varepsilon \varepsilon_0 E, \quad (1)$$

where S is the plate area; Q is the total charge on the plates; q is the specific charge on the plates; ε and ε_0 are the relative permittivity of the material and the permittivity of vacuum, respectively; E is the strength of the electric field created by the charges in the dielectric volume.

In reality, one can certainly expect the influence of a particular spatial distribution of charges both in the dielectric volume and in the solution layer directly wetting the charged dielectric (double electric layer), at least for the cases of small-sized structures. For this reason, more accurate calculations of real distributions will require taking into account

the spatial distribution of charges in the volumes of the contacting phases. If we take a typical value of the dielectric permittivity of SiO₂ in the range of 3.7–3.9, such an estimate gives a charge density of 3.3–3.5 $\mu\text{C}\cdot\text{cm}^{-2}$ at an electric field strength of 1000 $\text{V}\cdot\mu\text{m}^{-1}$ (a value close in order to the dielectric strength of silicon dioxide). The obtained value of the specific charge will be a minimum estimate of the dose required to implement the described lithography mechanism. Of course, the real value may differ significantly from this rough estimate due to a number of factors: incomplete use of the charge transferred by the electron beam (charge runoff, reflection and generation of secondary electrons), the structure of the oxide layer, the composition and conditions of development, etc. However, even from a preliminary rough estimate, one can conclude that there are prospects for a significant improvement in the dose characteristics of SiO₂ and materials based on it as a resist for electron beam lithography. It is also worth mentioning the paper [13], in which the authors present the results of experiments on the formation of graphene-like microstructures on SiO₂ films (obtained by thermal oxidation) after their exposure to an electron beam. According to the data presented in this paper, sensitivity at the level of hundreds of $\mu\text{C}\cdot\text{cm}^{-2}$ or better was achieved. The authors of this paper particularly note that the possibility of the mechanism of inducing the growth of graphene-like structures due to the phenomenon of contamination in the described experiments was excluded, and thus, the most probable mechanism of latent image formation is precisely the local charging of the SiO₂ layer. In general, it can be noted that despite the fact that the process of electron-beam lithography on SiO₂ has been studied for a very long time, many details of the processes taking place are still unknown. Moreover, some characteristics of the process are still unknown (in particular, the resolution at low electron energies).

The main goal of the presented work is to identify the main factors influencing the characteristics of the process of direct electron-beam lithography on SiO₂ films at electron energies within 10 keV.

2. Materials and Methods

2.1. Source materials and reagents

All experiments on electron-beam lithography described in this work were carried out on SiO₂ films with a thickness of 100–130 nm and 4.0 μm , which

were grown by thermal oxidation on substrates made of single-crystal silicon with the orientation $\langle 100 \rangle$.

The exposure of SiO₂ films was carried out on an electron-beam lithography of the E-Line series by Raith.

Aqueous solutions of dilute hydrofluoric acid with a volume ratio of components HF (47 % by weight) : NH₄F (40 % by weight) : H₂O (distillate) equal to 1 : 6 : 93 were used as the developer.

2.2. Film application and property determination methods

The metal films were deposited by magnetron sputtering on a 208HR Cressington setup. The nanostructures formed during lithography were studied by atomic force microscopy (AFM) on an NT-MDT Ntegra Prima AFM and transmission electron microscopy (TEM) on a Jeol JEM-2100 Plus TEM.

Numerical modeling of the electron penetration depth in the broad beam approximation for 130 nm and 4 μm thick SiO₂ films with a 12 nm thick protective copper coating was performed in CASINO version 2.48.

3. Results and Discussion

3.1. Exposure of SiO₂ films without additional preparation

In the first series of experiments, silicon wafers were used after oxidation without any additional treatment, except for cleaning in solvents (rinsing in acetone and isopropanol). In these experiments, SiO₂ films (100–130 nm thick) were exposed to an electron beam with subsequent development in a solution of dilute buffered hydrofluoric acid. Samples of the exposed SiO₂ film were studied using an AFM and an optical microscope before and after the development process. For such samples, darkening of the SiO₂ film color was observed in the exposed areas (starting with doses of several $\mu\text{C}\cdot\text{cm}^{-2}$). In addition, characteristic changes were observed in the nature of the surface relief of the film in the exposed areas after development. The appearance of the relief after development in many cases can be described as a “sponge” protruding above the surface surrounded by a uniformly etched oxide film. These changes in the relief can be explained by incomplete masking of the SiO₂ surface (due to numerous defects in such “masking”). In this case, the “pores” of such a spongy structure can extend below the level of the surrounding unexposed oxide. Another feature of

exposed structures on such samples is the frequently observed blurring of the exposure zone due to the formation of electrically charged areas inside the oxide film and the distortion of the electron trajectory during exposure. Observation of the above-described spongy structures with high surface roughness clearly indicates the presence of the so-called contamination of the oxide surface during electron beam exposure. This phenomenon radically worsens the quality of direct electron beam lithography on SiO_2 , and for exposure doses of tens of $\text{mC}\cdot\text{cm}^{-2}$ and higher makes such lithography completely impossible without taking special measures. The influence of this factor on the resolution of the direct electron beam lithography process on SiO_2 films is noted in the previously mentioned works, for example [1, 2, 11]. The phenomenon itself has been known and studied for a long time, since it often interferes with the electron microscopy process [14]. The generally accepted mechanism for the formation of contaminant deposits is the decomposition of adsorbed organic compounds (e.g., hydrocarbons from the lubricant of a pump system). In terms of the composition of the decomposition products, there are different opinions – from polymer compounds [15] to various carbon films [16–19]. Despite the fact that the question of the nature of contaminant deposits has a long history, there is still no complete understanding of the mechanism of their formation, as well as their composition and structure, despite examples of the successful application of this phenomenon for the formation of microstructures [20].

A common method of combating this phenomenon is to treat the surface of the exposed SiO_2 film in oxygen plasma. This is what the authors of [11] used. However, this approach has certain drawbacks associated with the relatively harsh physical impact on the oxide film in oxygen plasma. In addition to the chemical effect of oxygen plasma on contamination traces, a process of reactive ion sputtering of the oxide film material is possible, which in principle can affect the characteristics of the lithography process (for example, the residual roughness of the film and the resolution of the lithography process).

During the described experiments, it was noted that the contamination phenomenon is especially strong at low electron energies (the first few keV). It is also worth noting the extreme chemical stability of contamination spots in the exposure zones – they did not disappear even when exposed to a mixture of concentrated nitric and sulfuric acids when heated to 80°C for several minutes. It is noteworthy in connection with the fact that such a mixture of acids

is used in the processes of nitration of aromatic hydrocarbons and oxidation of graphite. For this reason, it can be assumed that the nature of the resulting contamination spots is not associated with simple adsorption and/or decomposition to carbon residue under the action of an electron beam of traces of organic impurities that may be present in very small quantities in the vacuum chamber during sample exposure.

3.2. Elimination of SiO_2 contamination of films exposed to metal coatings

To avoid the influence of contamination, further experiments were carried out on samples with SiO_2 films, onto which thin (about 10–15 nm) layers of various metals (copper, platinum, tungsten) were applied by magnetron sputtering. The main idea of this approach is to remove contamination spots formed during exposure before development together with the underlying sacrificial layer of metal. The choice of metal films as protective coatings is also due to the fact that they are able to effectively eliminate the manifestations of the charge accumulated by the dielectric oxide layer under the action of the electron beam (the “charging” effect). The main conclusion from the experiments with various metal coatings is that the efficiency of eliminating the influence of contamination spots depends on the nature of the metal used. Thus, for tungsten, contamination spots had significantly greater chemical resistance than in the case of copper or platinum. This conclusion was made from experiments in which the tungsten film was etched in a mixture of aqueous solutions of H_2O_2 and NH_3 after exposure – strong contamination spots on the tungsten were almost not affected by this mixture, despite the fact that the original tungsten film was completely removed in less than 5 min. In addition, these spots also had significant mechanical resistance to abrasion, which follows from the observation of their preservation even after intensive wiping of the sample with a cotton swab moistened with acetone (the original tungsten film is mostly removed from the surface of the sample under similar conditions). In the case of copper and platinum films, no fundamental difference in the chemical resistance of the films in the contamination zones compared to the unirradiated areas was observed. Thus, copper films are completely removed together with contamination spots in solutions of dilute nitric acid in a few minutes. The set of observations made during the experiments allows us to suggest that the nature of contamination on different materials may be different

(at least there are two alternatives). For SiO_2 and tungsten, the nature of contamination spots can be associated with the formation of very thin layers of carbides (or other carbon-containing, carbide-like compounds) of the corresponding element. Some carbides (such as SiC and W_xC) are known for their chemical resistance and that is why they can work as a mask during the development process. Metals such as copper and platinum do not form stable carbides, for this reason the nature and properties of contamination spots for them will be different than for materials based on carbide-forming elements.

3.3. Determination of the dose dependence of the depth of structures formed in the SiO_2 layer using direct electron beam lithography

For experiments on determining the dose dependence of the depth of structures formed in the SiO_2 layer using the direct electron beam lithography method, samples with SiO_2 films on single-crystal silicon wafers (with an oxide thickness from 100 nm to 4 μm , obtained by thermal oxidation of the silicon substrate with the $\langle 100 \rangle$ orientation) and a metal layer (copper or platinum, 10–15 nm thick) deposited on the oxide were used. Such layers were chosen as protective sacrificial layers because they demonstrated the effectiveness of protection against contamination and the charging phenomenon. Figure 1 shows images of the surface relief of a developed sample with an example of contamination (without a protective sacrificial copper layer) and with a protective coating (R_a is the average roughness).

A diluted buffered hydrofluoric acid solution with a volume ratio of HF (47 % by weight) : NH_4F

(40 % by weight) : H_2O (distillate) components equal to 1 : 6 : 93 (similar to that used in [11]) was used as a developer. The development time was from 3 to 10 min, the temperature was 21 °C. Thus, the conditions of the experiments carried out allow us to compare the results obtained in this work with the results described in the paper [11]. It can be noted that the qualitatively obtained results are in agreement with the data of [11] – an increase in the depth of structures in the dose range up to the first hundreds of $\text{mC}\cdot\text{cm}^{-2}$ and then reaching a constant value. A significant, although expected, difference is a decrease in the dose sensitivity of the process by approximately 2–3 times compared to the data of [11]. This decrease is expressed in a less sharp dependence of the depth of the obtained structures on the exposure dose, and a shift in the dose of the output at a constant (maximum) depth towards higher dose values. In addition, in contrast to work [11], the maximum sensitivity to the action of the electron beam occurred at high values of electron energy – in the range of 3–6 keV. All these results, at least at a qualitative level, are quite expected, since they are obviously associated with the shielding effect of the protective metal layer. However, compared with the data of work [11], the results obtained in this work allow us to make a significant clarification – the initial section of the dose dependence of the depth of the structures on the exposure dose is not linear, but more complex. In general, the dependence of the depth of the formed structures observed in our experiments can be described quite accurately by the following empirical S-shaped dependence (2):

$$h(D) = h_{\text{sat}} \frac{D^n}{D^n + D_{h/2}^n}, \quad (2)$$

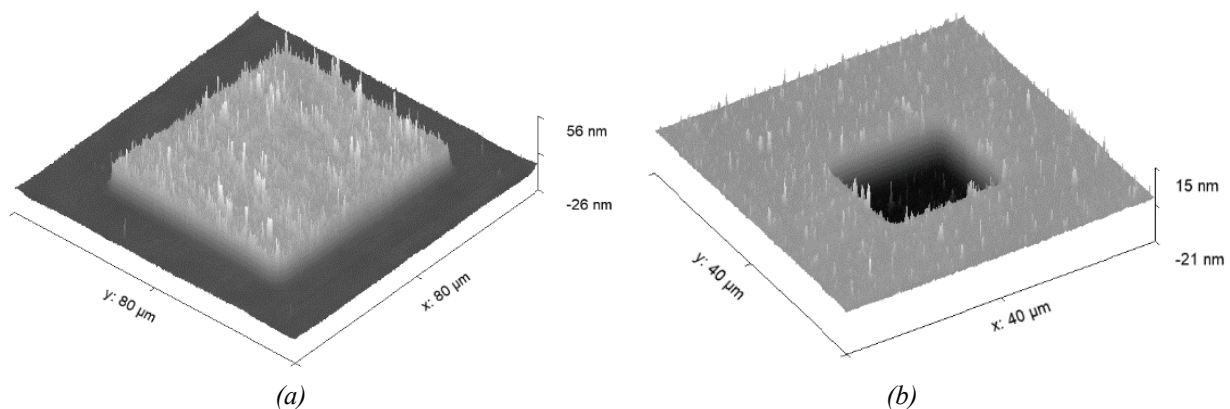


Fig. 1. Surface relief of exposed and developed samples (according to AFM data):

a – without using a 12 nm protective copper layer at the exposure stage (in the exposed region $R_a = 2.5\text{--}3.8$ nm);

b – with a protective layer (in the exposed region $R_a = 1.7$ nm).

The average value of the SiO_2 surface roughness after development in unexposed regions $R_a = 0.3\text{--}0.7$ nm

where h_{sat} is a factor that specifies the maximum (for a given electron energy and development conditions) depth of the structures being formed, i.e. a depth limitation for the case of obviously large exposure doses (the “saturation” region); D is the exposure dose; $D_{h/2}$ is the dose corresponding to half of the maximum depth of the structures; n is an empirical factor that determines the degree of nonlinearity of the given dependence.

For the case of small exposure doses, this dependence can be simplified to a power dependence of the form (3):

$$h(D) = k D^n, \quad (3)$$

where k is the coefficient of proportionality, it is obvious that at $D \ll D_{h/2}$, $k \rightarrow h_{\text{sat}} / D_{h/2}^n$. This type of dependence can be useful, for example, for cases of high electron energies in the beam, when the value of $D_{h/2}$ is large and the applied exposure doses are obviously lower than this value. According to the experimental results, all the specified parameters show a dependence on the presence of a protective layer and on the development conditions. The experiments also show that they depend to a much lesser extent on the thickness of the SiO_2 layer (practically only in the form of a dependence on the duration of time between exposure and development).

From the given dependences (experiment and approximation), it is evident that there is an initial section of the dependence corresponding to a weak increase in depth with increasing dose and a section of reaching an almost constant value. Accordingly, the steepness of the dose dependence in the sections before “saturation” is not constant, but has

a maximum in the region of average values of exposure doses. Based on this result, it can be assumed that this feature can be used to improve the dose sensitivity of the process, at least in some cases, for direct electron-beam lithography on SiO_2 , by additional uniform exposure of the entire sample area with an electron beam – before or after exposure of the structures themselves.

Also, within the framework of this work, studies on the dependences of the depth of the structures obtained during lithography on exposure doses on much thicker SiO_2 films (4 μm) were conducted. In the course of these studies, it was found that the general nature of the dependence of the depth of the structures after development has the same character as on thin (130 nm) SiO_2 films (Fig. 2).

However, the quantitative ratios for a 4 μm oxide film are somewhat different from those for 100–130 nm oxide films for electron energies greater than 6 keV. In addition, an important feature was discovered for 4 μm films: if the film was developed not within the next 4 hours after exposure, but after 3 days, the depth of the structures formed during development was significantly greater (Fig. 3).

In other words, processes that increase the average rate of its etching in a dilute solution of buffered hydrofluoric acid (at least in the first 3 days) occur in SiO_2 exposed to an electron beam, when stored at room temperature. For thin SiO_2 films (130 nm), a similar phenomenon of increasing the exposure efficiency after holding the samples (before the development of the latent image of the structures) was observed only for low electron energies (1.5 keV) and to a significantly lesser extent (Fig. 4).

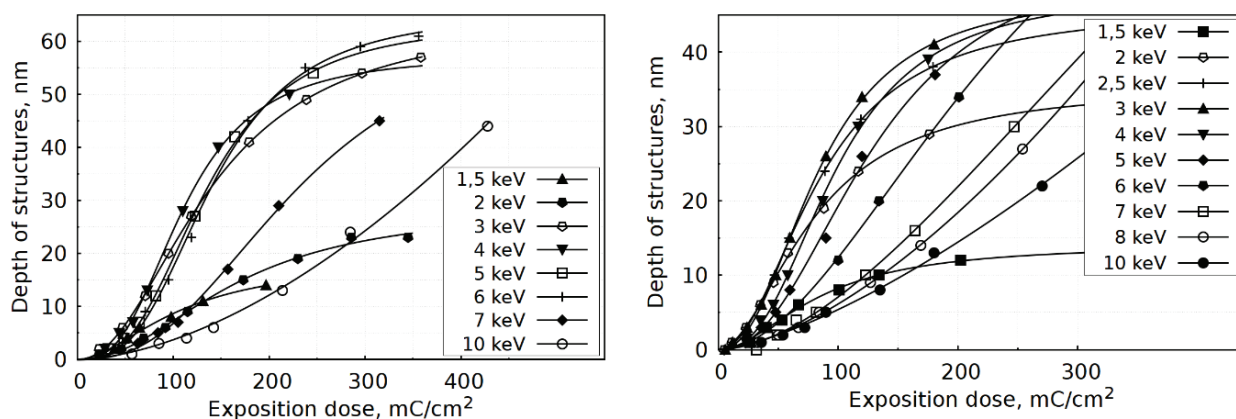


Fig. 2. Dependences of the depth of structures formed in the oxide during 3 min of development (less than 4 hours after exposure) in a solution of diluted buffered hydrofluoric acid on the exposure dose.

The initial thickness of the SiO_2 layer in the graph on the left is 130 nm, on the right – 4 μm (in all cases, a protective copper coating with a thickness of 12 nm was used during exposure)

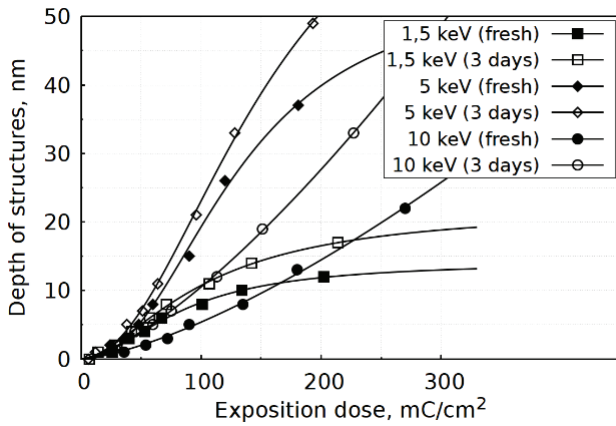


Fig. 3. Dependences of the depth of structures formed in SiO₂ (4 μm thick) during 3 min of development, for cases of development immediately (less than 4 hours) and 3 days after exposure (in all cases, a protective coating of 12 nm copper was used during exposure)

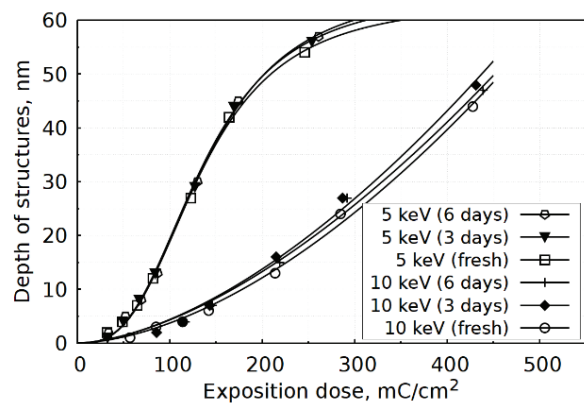
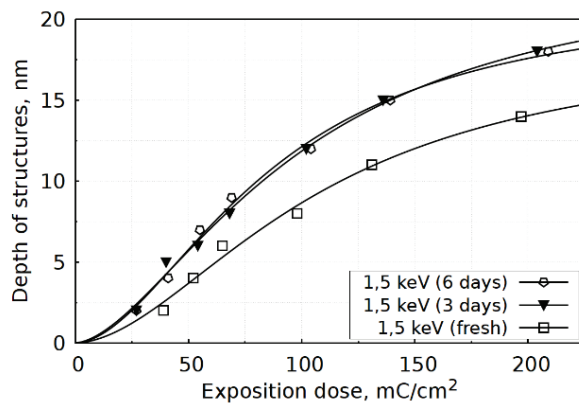


Fig. 4. Dependences of the depth of structures formed in SiO₂ (130 nm thick) after 3 min of development, for cases of development immediately (less than 4 hours), after 3 days and after 6 days after exposure (in all cases, a protective coating of 12 nm copper was used during exposure)

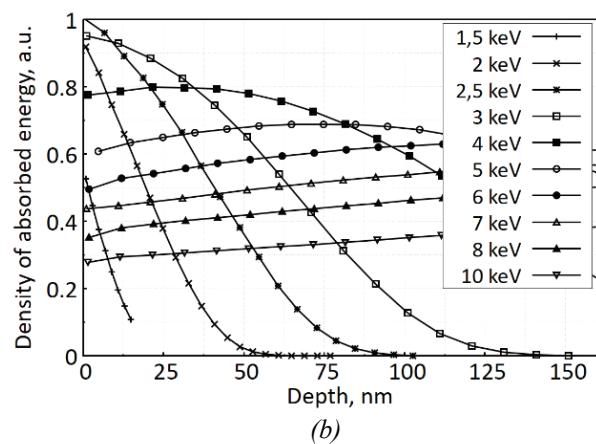
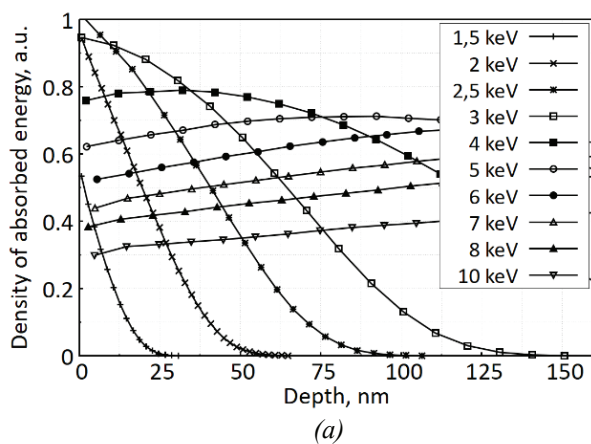


Fig. 5. Distributions of specific energy losses by electrons according to modeling (in the same relative values on all graphs) by the volume of the SiO₂ layer (taking into account the influence of the overlying protective layer of 12 nm copper) depending on the depth of the corresponding layer:
a – for a SiO₂ layer of 130 nm; b – 4 μm

It is worth noting that for the indicated cases (for SiO₂ films with a thickness of 130 nm and 4 μm, with a protective copper coating of 12 nm), numerical modeling was carried out in the broad beam approximation, which showed that the distributions of specific energy losses by electrons (per unit volume) in a silicon dioxide layer under the same protective copper layer are practically independent of the thickness of the SiO₂ layer (Fig. 5).

This simulation result is consistent with the experiments for oxide films of different thicknesses and also indicates the need to expand and refine the model used to describe the processes occurring during irradiation of the oxide layer by an electron beam. At the same time, a comparison of the simulation results and experimental data confirms the conclusions of the paper [11] on the determining role of the electron penetration depth, for cases of low

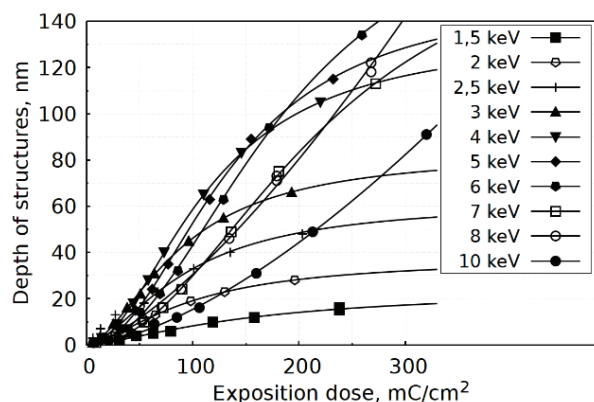


Fig. 6. Dependences of the depth of structures formed in SiO₂ (4 μm thick) during 10 min of development, for cases of immediate development (less than 4 hours)

energies, to the maximum depth of the structures formed during development (parameter h_{sat} in the equation of the S-shaped dependence given above). Thus, for electron energies up to 2 keV, no significant difference is observed in the depth of the structures formed for either 3 min of development or 10 min of development (Fig. 6).

This fact is easily explained if we take into account that for low electron energies, the area of their impact on the oxide layer is limited in depth. With further etching of the underlying layers, there will be no additional difference in the amount of dissolved oxide. Reaching the maximum depth of the structures for large exposure doses in the experiments described in this paper is also consistent with the observations of [11] on the existence of a maximum value of the acceleration factor for the etching of the exposed oxide. For the etching rate measured in the described experiments (about 7.1 nm·min⁻¹ for SiO₂ in the above solution of diluted buffered hydrofluoric acid at 21 °C), the acceleration factor reaches a value of about 2.9 and higher, which indicates a sufficiently high efficiency of oxide protection from contamination by the copper layer.

All parameters of the approximating dependences of the depth of the formed structures on the exposure dose (structures in the form of homogeneous areas) presented in the graphs in this paper are given in Table 1.

Table 1. Parameters of approximating dependences of the depth of formed structures on the exposure dose

Thickness of SiO ₂	Electron energy, keV	Exposure time (dash – less than 4 h), 24 h	Development time, min	Parameters of the approximating dependence for the depth of structures		
				h_{sat}	$D_{h/2}$, mC·cm ⁻²	n
1	2	3	4	5	6	7
130 nm	1.5	–	3	18.6	108	1.82
130 nm	2.0	–	3	28.5	164	2.15
130 nm	3.0	–	3	64.6	139	2.13
130 nm	4.0	–	3	57.3	111	2.85
130 nm	5.0	–	3	63.7	134	2.91
130 nm	6.0	–	3	65.5	140	2.99
130 nm	7.0	–	3	66.8	236	2.54
130 nm	10.0	–	3	$k = 0.00143$		1.71
130 nm	1.5	3	3	23.4	99	1.67
130 nm	1.5	6	3	21.4	86	1.83
130 nm	5.0	3	3	65.2	135	2.91
130 nm	5.0	6	3	66.3	138	2.90
130 nm	10.0	3	3	$k = 0.00220$		1.65
130 nm	10.0	6	3	$k = 0.00238$		1.63
4,0 μm	1.5	–	3	14.2	84	1.90
4,0 μm	2.0	–	3	35.5	80	1.90
4,0 μm	2.5	–	3	45.9	85	2.11

Continuation Table 1

1	2	3	4	5	6	7
4,0 μm	3.0	—	3	48.2	84	2.33
4,0 μm	4.0	—	3	48.1	98	2.54
4,0 μm	5.0	—	3	54.7	130	2.30
4,0 μm	6.0	—	3	89.7	260	1.92
4,0 μm	7.0	—	3	147	526	1.80
4,0 μm	8.0	—	3	$k = 0.00408$		1.59
4,0 μm	10.0	—	3	$k = 0.00757$		1.43
4,0 μm	1.5	—	10	24.0	157	1.45
4,0 μm	2.0	—	10	37.4	97	1.57
4,0 μm	2.5	—	10	62.2	93	1.65
4,0 μm	3.0	—	10	83.3	88	1.72
4,0 μm	4.0	—	10	134	114	1.95
4,0 μm	5.0	—	10	152	135	2.12
4,0 μm	6.0	—	10	203	188	2.08
4,0 μm	7.0	—	10	190	225	2.07
4,0 μm	8.0	—	10	$k = 0.0487$		1.40
4,0 μm	10.0	—	10	$k = 0.0137$		1.53
4,0 μm	1.5	3	3	22.0	103	1.67
4,0 μm	5	3	3	81.6	158	2.05
4,0 μm	10	3	3	$k = 0.0170$		1.40

3.4. Determination of the resolving power of direct electron beam lithography on SiO₂ using an electron beam with low electron energies

One of the objectives of this work was to determine the resolving power of direct electron-beam lithography on SiO₂ using an electron beam with low (within 10 keV) electron energies. These experiments were performed on samples with a SiO₂ layer thickness of about 130 nm and an additional copper layer of 12 nm (magnetron sputtering). To test the resolving power of the process, sets of structures in the form of parallel lines and dot arrays with different periods were used. The exposure parameters were: electron energy of 10 keV at doses from 30 to 480 nC·cm⁻¹ for structures in the form of parallel and intersecting lines and from 0.075 to 1.2 pC for a dot array. After exposure, the copper layer was removed using a dilute (about 20 wt. %) nitric acid solution (etching for 3 min). The actual development of the latent image was carried out in an aqueous solution of diluted buffered hydrofluoric acid with a volume ratio of the initial components HF (aqueous solution 47 % by weight) : NH₄F (aqueous solution 40 % by

weight) : H₂O equal to 1 : 6 : 93. The test structures obtained after the development of the latent image were studied using atomic force microscopy methods (Figs. 7, 8).

In addition, for some of the structures obtained in the described process, TEM-images (Fig. 9) of their cross sections shown in the figure below were obtained. These images allow a more accurate assessment of the characteristics of the described lithography process.

The obtained images of the structures (Figs. 7–10) allow us to say that the resolution of the described lithography process is in all cases no worse than 30 nm (in half-step resolution for a set of lines). Figure 9 shows the profile for widely spaced parallel lines, and Fig. 10 shows the profiles for lines with a period of 60 nm (the densest arrangement, at which the proximity effect is not yet noticeably evident). The TEM (the most accurate characteristic of the resolution) and AFM (a more rapid assessment, since it does not require special sample preparation) data provide a consistent assessment of the resolution of the described lithographic process.

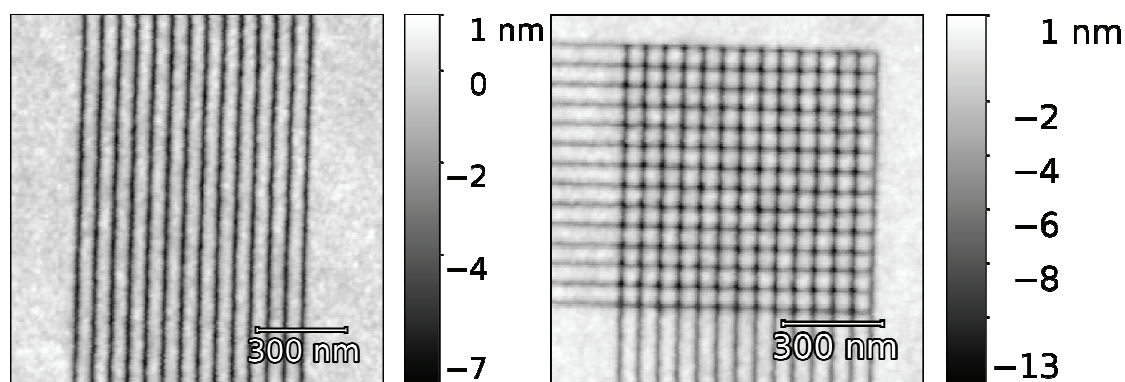


Fig. 7. AFM-images of developed structures in the form of parallel and intersecting lines (with a period of 60 nm) obtained by exposing (linear dose $480 \text{ nC}\cdot\text{cm}^{-1}$) a 130 nm SiO_2 film (12 nm protective Cu layer) and developing for 3 min in dilute buffered hydrofluoric acid

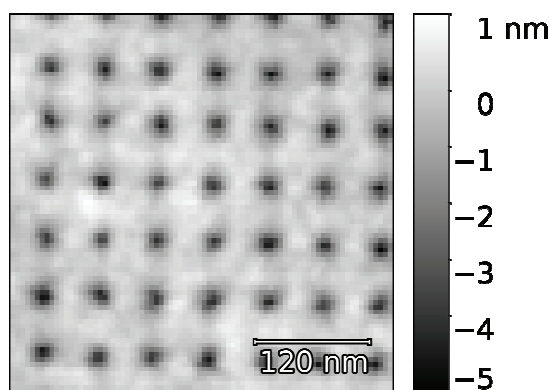


Fig. 8. AFM-images of developed structures in the form of an array of dots (with a period of 60 nm) obtained by exposing (dose 1.2 pC per dot) a 130 nm SiO_2 film (12 nm protective Cu layer) and developing for 3 min in dilute buffered hydrofluoric acid

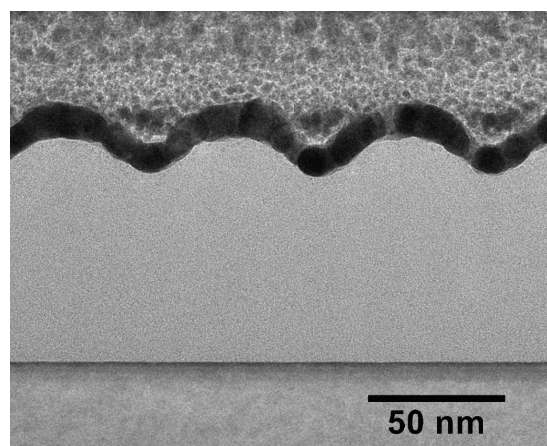


Fig. 10. TEM-images of cross-section of parallel line structures (period 60 nm). SiO_2 layer initial thickness 130 nm (Cu protective layer 12 nm) developed for 3 min in dilute buffered hydrofluoric acid (linear dose $480 \text{ nC}\cdot\text{cm}^{-1}$)

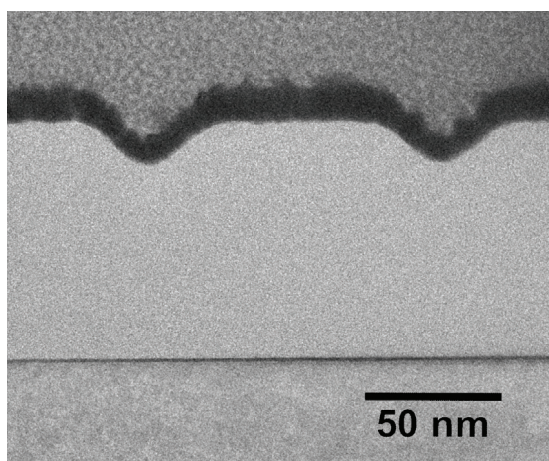


Fig. 9. TEM-images of cross-section of parallel line structures (period 120 nm). SiO_2 layer initial thickness 130 nm (Cu protective layer 12 nm) developed for 3 min in dilute buffered hydrofluoric acid (linear dose $480 \text{ nC}\cdot\text{cm}^{-1}$)

The following assessment criteria were used: the line profile according to the TEM data and the relief data of the structures from AFM (based on the coincidence of the oxide levels at the tops of the ridges between the line depressions and the level in the unexposed area of the SiO_2 film). When forming nanostructures in the form of individual dots, a resolution of no worse than 25 nm (according to the width of the transverse profile at half the depth) was achieved.

4. Conclusion

The effects of contamination and charging during exposure of SiO_2 films to an electron beam are particularly pronounced when using relatively low electron energies, especially in the range of keV units. The nature of contamination has a clear

dependence on the composition of the upper layers. A correlation between the ability of the elements constituting the upper layers to form stable carbides and the chemical stability of contamination spots has been noted. These phenomena, which have a strong effect on the process of developing a latent image, can be effectively eliminated even by thin (10–15 nm) sacrificial layers of metals that do not form stable carbides (for example, copper or platinum).

The dose dependences of the depth of developed structures for the process of direct electron beam lithography on SiO₂ have an S-shape with an area of greatest growth at average dose values and subsequent reaching the maximum depth value. Based on the described dose dependence, it is possible to propose a method for increasing the effective sensitivity of the described lithography process by additional uniform exposure of the SiO₂ layer to the electron beam. The characteristic (primarily for thick SiO₂ films) increase in the depth of structures during the first 3 days after exposure suggests the presence of several mechanisms or stages of the process of forming latent images in the SiO₂ layer. Experimental data clearly indicate the presence of processes occurring in the “activated” areas of SiO₂ after the electron beam has ceased to act. As a hypothesis explaining the mechanism of these processes at a qualitative level, it is possible to propose the process of draining volume charges from the exposed areas.

The issue of the dependence of the depth of structures on the time elapsed since the moment of exposure is of great interest, since it has previously been almost never considered in the literature and requires further more detailed study from the point of view of establishing the mechanisms of the processes occurring in SiO₂ films, both during and after their exposure to electrons. This information, together with the temperature dependence (an estimate of the activation energy of processes in the film after exposure) can provide valuable information on the kinetics of the processes taking place.

The resolution (not worse than 30 nm) achieved in the described processes of electron-beam lithography on SiO₂ as a sensitive layer allows us to talk about the possibility of their application in the production of certain nanostructures, in particular nanopores.

5. Supplementary Material

The data is contained in the paper or additional material located at: <https://disk.yandex.ru/d/c5M2GacXmpkGJg>

6. Funding

The work was supported by project No. FFFG-2025-0001 of the Ministry of Science and Higher Education of the Russian Federation. The experimental investigations were performed in the Institute of Nanotechnology of Microelectronics of the Russian Academy of Sciences (INME RAS) Large Scale Research Facility Complex for Heterogeneous Integration Technologies and Silicon + Carbon Nanotechnologies.

7. Conflict of interest

The authors declare no conflict of interest.

References

1. Allee DR, Umbach CP, Broers AN. Direct nanometer scale patterning of SiO₂ with electron-beam irradiation. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*. 1991;9(6):2838-2841. DOI:10.1116/1.585652
2. Allee DR, Broers AN. Direct nanometer scale patterning of SiO₂ with electron beam irradiation through a sacrificial layer. *Applied Physics Letters*. 1990;57(21):2271-2273. DOI:10.1063/1.103909
3. Gorwadkar S, Wada T, Shirakashi JI, Hiroshima H, et al. Development of SiO₂/c-Si bilayer e-beam resist process and its application for 10-nm-scale MIM junctions. In: Vladimirsky Y. (eds.) *23rd Annual International Symposium on Microlithography* Santa Clara: SPIE; 1998. p. 359. DOI:10.1117/12.309591
4. Wada T, Haraichi S, Ishii K, Hiroshima H, et al. SiO₂/poly-Si electron beam resist process for nanofabrication. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 1996;14(3):1850-1854. DOI:10.1116/1.580348
5. Pan X, Allee DR, Broers AN, Tang YS, et al. Nanometer scale pattern replication using electron beam direct patterned SiO₂ as the etching mask. *Applied Physics Letters*. 1991;59(24):3157-3158. DOI:10.1063/1.105770
6. Pan X, Broers A. Nanometer scale pattern generation in deposited SiO₂ with electron beam irradiation. *Journal of Applied Physics*. 1992;71(12):6189-6191. DOI:10.1063/1.350429
7. Pan X, Broers AN. Improved electron beam pattern writing in SiO₂ with the use of a sample heating stage. *Applied Physics Letters*. 1993;63(10):1441-1442. DOI:10.1063/1.109650
8. Haraichi S, Wada T, Gorwadkar SM, Ishii K, et al. Electron beam dot lithography for nanometer-scale tunnel junctions using a double-layered inorganic resist. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*. 1997;15(4):1406-1410. DOI:10.1116/1.589549
9. Wada T, Haraichi S, Ishii K, Hiroshima H, et al. The use of a Si-based resist system and Ti electrode for the fabrication of sub-10 nm metal-insulator-metal tunnel

junctions. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 1998;16(3):1430-1434. DOI:10.1116/1.581163

10. Pennelli G, Totaro M, Piotto M. Selective doping of silicon nanowires by means of electron beam stimulated oxide etching. *Nano Letters*. 2012;12(2):1096-1101. DOI:10.1021/nl2045183

11. Beaumont A, Dubuc C, Beauvais J, Drouin D. Direct-write electron beam lithography in silicon dioxide at low energy. *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*. 2010;28(5):940-945. DOI:10.1116/1.3478304

12. Knyazev MA, Sedlovets DM, Trofimov OV, Redkin AN. The influence of the electron-beam exposure of SiO₂/Si and quartz substrates on the selective growth of graphene-like films. *Materials Research Bulletin*. 2017;86:322-326. DOI:10.1016/j.materresbull.2016.11.007

13. Santiago Neto RB, Lesche B. Electric field assisted hydrogen fluoride etching of silica. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*. 2009;465(2111):3447-3462. DOI:10.1098/rspa.2009.0216

14. Vldar A, Postek M. Electron beam-induced sample contamination in the SEM. *Microscopy and Microanalysis*. 2005;11(S02). DOI:10.1017/S1431927605507785

15. Ennos AE. The origin of specimen contamination in the electron microscope. *British Journal of Applied Physics*. 1953;4(4):101-106. DOI:10.1088/0508-3443/4/4/302

16. Luo JS, Sung CS, Hsu WS, Huang LY, et al. Electron beam induced carbon deposition using hydrocarbon contamination for XTEM analysis. *Microelectronics Reliability*. 2010;50(9-11):1446-1450. DOI:10.1016/j.microrel.2010.07.046

17. Orekhova KN, Serov YuM, Dement'ev PA, Ivanova EV, et al. Investigation of a contamination film formed by the electron beam irradiation. *Technical Physics*. 2019;64(9):1336-1342. DOI:10.1134/S1063784219090123

18. Hugenschmidt M, Adrion K, Marx A, Müller E, et al. Electron-beam-induced carbon contamination in STEM-in-SEM: quantification and mitigation. *Microscopy and Microanalysis*. 2023;29(1):219-234. DOI:10.1093/micmic/ozac003

19. Hettler S, Dries M, Hermann P, Obermair M, et al. Carbon contamination in scanning transmission electron microscopy and its impact on phase-plate applications. *Micron*. 2017;96:38-47. DOI:10.1016/j.micron.2017.02.002

20. Schiffmann KI. Investigation of fabrication parameters for the electron-beam-induced deposition of contamination tips used in atomic force microscopy. *Nanotechnology*. 1993;4(3):163-169. DOI:10.1088/0957-4484/4/3/006

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Received 16 January 2025; Revised 24 February 2025; Accepted 28 February 2025



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