

FABRICATION OF SUB-MICRON ETCH-RESISTANT
METAL/SEMICONDUCTOR STRUCTURES USING
RESISTLESS ELECTRON BEAM LITHOGRAPHY

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BACKGROUND OF THE INVENTION

1. Field of the invention:

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The present invention relates to a method using resistless electron beam lithography for fabricating masks for X-ray and/or ultraviolet lithography, and for fabricating molds for imprint lithography.

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2. Brief description of the prior art:

The fabrication of ultra-small scale electronic devices requires efficient high resolution lithography techniques. Resist-based lithography processes are very frequently involved in these high resolution lithography techniques, and poly(methyl methacrylate) (PMMA) is the polymer most widely used as a resist for electron beam lithography applications (S. P. Beaumont, P. G. Bower, T. Tamamura, C. D. W. Wilkinson, *Appl. Phys. Lett.*, **38**, 438 (1991) and W. Chen, H. Ohmed, *J. Vac. Sci. Technol.*, **B 11**, 2519 (1993)).

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These types of lithographic processes suffer from several limitations which can become extremely constraining in the fabrication of sub-100 nm devices. These limitations include undesirable proximity effects in the resist and resolution limits imposed by the size of the polymer molecules. Proximity effects are produced when the exposed patterns are situated within the range of backscattered electrons. These electrons are primary electrons which collide with the substrate with a great angle to escape from the surface with a high energy in an area which may be considerably larger than the electron beam diameter. These high energy electrons expose the resist in an undesirable region. Current research efforts in lithography techniques include several resistless processes for defining patterns (see for example D. Wang, P. C. Hoyle, J. R. A. Cleaver, G. A. Porkolab, N. C. MacDonald, *J. Vac. Sci. Technol.*, **B 13**, 1984 (1995) for electron beams; and H. Sugimura and N. Nakagiri, *J. Vac. Sci. Technol.*, **B 13**, 1933 (1995) for a scanning probe technique).

The formation of a silicide layer is usually carried out by annealing samples of thin metal layers on silicon substrates in a conventional furnace with a controlled atmosphere of N_2-H_2 . This annealing technique requires several minutes to convert the metal film into silicide (see C. A. Chang, *J. Appl. Phys.*, **58**, 3258 (1985); C. A. Chang and A. Segmuller, *J. Appl. Phys.*, **61**, 201 (1987); C. A. Chang and W. K. Chu, *Appl. Phys. Lett.*, **37**, 3258 (1980); and C. A. Chang and J. M. Poate, *Appl. Phys. Lett.*, **36**, 417 (1980)).

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New techniques involving Rapid Thermal Annealing (RTA) improve the process of the formation of silicide. RTA silicide films

are significantly better than those formed by conventional annealing (C. A. Dimitriadis, *Appl. Phys. Lett.*, **56**, 143 (1990)), due to a shorter processing time (A. Torres, S. Kolodinski, R. A. Donaton, K. Roussel and H. Bender, *SPIE*, **2554**, 185 (1995)).

5 More recently, several techniques of formation of silicide
have been developed. These processes involve heating of metal-silicon
interfaces using photons, electrons and ion beams (J. M. Poate and J. W.
Mayer, *Laser Annealing of Semiconductors*, Academic Press, New York,
1982; J. Narayan, W. L. Brown and R. A. Lemons, *Laser-Solids*
10 *Interactions and Transient Processing of Materials*, North-Holland, New
York, 1983; and E. D'Anna, G. Leggieri and A. Luches, *Thin Solids Films*,
129, 93 (1985)). All these processes are based on the concept of forming
silicide with localized heating near the surface. However, none of these
techniques are intended as lithography processes or for the fabrication of
15 masks for lithography.

Ultraviolet (UV) lithography is the technique used in large scale production of devices and circuits. However, the wavelength of ultraviolet light represents a physical limit to the resolution that can be achieved using this technique. Alternative techniques are being evaluated to replace UV lithography for industrial production of electronic devices and circuits. One of these techniques is X-ray lithography, since X-rays have a much smaller wavelength than UV. In this technique, regions of a mask placed between the X-ray source and the sample are covered by a layer of heavy atoms (such as Ta, W and tantalum silicides) which absorbs X-rays (J. Canning, *Journal of Vacuum Science and Technology*, B15, 2109 (1997)). Such masks are fabricated using

electron-beam lithography. A major challenge in the fabrication of these masks is to use electron-beam lithography to form structures (etch masks) that have both a high resolution and an excellent resistance to chemicals employed to remove the absorbent layer of heavy atoms in unprotected regions. Conventional techniques using polymeric resists as
5 etch masks either do not provide a sufficient resolution or do not provide a sufficient resistance to chemical etching (J.P. Silverman, *Journal of Vacuum Science and Technology*, **B15**, 2117 (1997)).

10 OBJECTS OF THE INVENTION

An object of the present invention is therefore to overcome the above described drawbacks of the prior art.

15 Another object of the invention is to provide a direct write resistless lithography method capable of fabricating masks for X-ray and/or ultraviolet lithography.

20 A still further object of the invention is to provide a direct write resistless lithography method for fabricating molds usable for imprint lithography.

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SUMMARY OF THE INVENTION

The present invention relates to a method for fabricating a mask for X-ray and/or ultraviolet lithography, comprising providing a substrate made of material transparent to X-ray and/or ultraviolet radiation or reflective to ultraviolet radiation, depositing on the substrate a layer made of material opaque to X-ray and/or ultraviolet radiation, depositing on the layer of material opaque to X-ray and/or ultraviolet radiation two superposed layers including a layer of semiconductor material and a layer of metal capable of reacting with the semiconductor material to form an etch-resistant metal/semiconductor compound, producing a focused electron beam, applying the focused electron beam to the superposed layers of metal and semiconductor material to locally heat the metal and the semiconductor material and cause diffusion of metal and semiconductor material in each other to form etch-resistant metal/semiconductor compound, displacing the focused electron beam on the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound, and etching the layer of metal, the layer of semiconductor material and the layer of material opaque to X-ray and/or ultraviolet radiation to leave on the substrate the structure of etch-resistant metal/semiconductor compound and the layer of material opaque to X-ray and/or ultraviolet radiation underneath the structure of etch-resistant metal/semiconductor compound to thereby form the mask for X-ray and/or ultraviolet lithography.

According to a preferred embodiment, the layer of semiconductor material is deposited on the layer of material opaque to X-ray and/or ultraviolet radiation, and the layer of metal is deposited on the layer of semiconductor material. Alternatively, the layer of metal is deposited on the layer of material opaque to X-ray and/or ultraviolet radiation, and the layer of semiconductor material is deposited on the layer of metal.

In accordance with other preferred embodiments of the mask fabricating method:

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- the material transparent to X-ray and/or ultraviolet radiation comprises glass, silicon nitride, silicon carbide, silicon dioxide, and diamond film;

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- the material opaque to X-ray and/or ultraviolet radiation is selected from the group consisting of: tantalum, tantalum silicide, tungsten, tungsten silicide, titanium, chromium, nickel silicide, TaB₄, WB₄, chromium silicide, and nickel;

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- when the mask is a mask for X-ray lithography, the material opaque to X-ray radiation is selected from the group consisting of: tantalum, tantalum silicide, tungsten, tungsten silicide, TaB₄ and WB₄;

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- when the mask is a mask for ultraviolet lithography, the material opaque to ultraviolet radiation is selected from the group consisting of: tantalum, tantalum silicide, titanium, chromium, nickel silicide, chromium silicide and nickel;

- the semiconductor material comprises silicon and the metal is selected from the group consisting of: cobalt, chromium, hafnium, iridium, manganese, nickel, palladium, platinum, rhodium, tantalum, titanium, tungsten, zirconium, copper and silver; and

- 5 - displacing the focused electron beam on the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound comprises exposing each portion of the structure of etch-resistant metal/semiconductor compound to the focused electron beam once or a plurality of times.

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The present invention also relates to a method for fabricating a mold for imprint lithography, comprising providing a mechanically resistant substrate, depositing on the substrate two superposed layers including a layer of semiconductor material and a layer of metal capable of reacting with the semiconductor material to form etch-resistant metal/semiconductor compound, producing a focused electron beam, applying the focused electron beam to the superposed layers of metal and semiconductor material to locally heat the metal and semiconductor material and cause diffusion of the metal and semiconductor material in each other to form etch-resistant metal/semiconductor compound, displacing the focused electron beam onto the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound, and etching the layers of metal and semiconductor material to leave on the substrate only the structure of etch-resistant metal/semiconductor compound, wherein the structure or etch-resistant metal /semiconductor compound

forms an imprint of the mold and wherein the structure and substrate form the mold for imprint lithography.

According to a first preferred embodiment, the layer of semiconductor material is deposited on the substrate, and the layer of metal is deposited on the layer of semiconductor material. Alternatively, the layer of metal is deposited on the substrate, and the layer of semiconductor material is deposited on the layer of metal.

According to other preferred embodiments of the mold fabricating method:

- the substrate is made of a material selected from the group consisting of: clean silicon, silicon carbide, glass, quartz, tantalum, titanium, tungsten, tantalum silicide, tungsten silicide, TaB₄, and WB₄;

- the semiconductor material comprises silicon and the metal is selected from the group consisting of cobalt, chromium, hafnium, iridium, manganese, nickel, palladium, platinum, rhodium, tantalum, titanium, tungsten, zirconium, copper and silver;

- the focused electron beam is a highly focused electron beam;

- after etching the layers of metal and semiconductor material, a plasma etch is used to remove a carbon deposit formed at the surface of the structure of etch-resistant metal/semiconductor compound;

- displacing the focused electron beam on the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound comprises exposing each portion of the structure of etch-resistant metal/semiconductor compound to the focused electron beam once or a plurality of times; and

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- etching the layers of metal and silicon comprises plasma or wet etching the metal, and plasma or wet etching the silicon layer.

The objects, advantages and other features of the present invention will become more apparent upon reading of the following non restrictive description of preferred embodiments thereof, given by way of example only with reference to the accompanying drawings.

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BRIEF DESCRIPTION OF THE DRAWINGS

In the appended drawings:

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Figure 1a is a side elevational view of a silicon substrate on which a layer or film of metal has been deposited;

Figure 1b is a side elevational view of the silicon substrate and layer of metal of Figure 1a, showing annealing of the silicon substrate and layer of metal by means of a controlled and focused electron beam;

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Figure 1c is a side elevational view of the silicon substrate and layer of metal of Figure 1a, showing a silicide structure that has been formed on the silicon substrate;

5 Figure 1d is a side elevational view of the silicon substrate and layer of metal of Figure 1a, in which the non reacted portion of the layer of metal has been wet etched to leave on the silicon substrate only the silicide structure;

10 Figure 2a is a graph showing an Auger Electron Spectroscopy (AES) depth profile of a layer or film of platinum (Pt) deposited onto a silicon substrate;

15 Figure 2b is a graph showing an AES depth profile of a layer or film of platinum (Pt) deposited onto a silicon substrate, after an annealing treatment using an electron beam;

20 Figure 3a is a side elevational view showing a substrate, a deposited layer of substrate capable of absorbing X-ray and/or ultraviolet radiation, a deposited silicon layer and a deposited metal layer;

25 Figure 3b is a side elevational view of the substrate, deposited layer of substrate capable of absorbing X-ray and/or ultraviolet radiation, deposited silicon layer and deposited metal layer of Figure 3a, showing silicide formed by reaction between the silicon layer and the metal layer after an annealing treatment using a focused electron beam;

Figure 3c is a side elevational view corresponding to the side elevational view of Figure 3b, in which the metal layer has been etched;

5 Figure 3d is a side elevational view corresponding to the side elevational view of Figure 3c, in which the silicon layer has been etched;

10 Figure 3e is a side elevational view corresponding to the side elevational view of Figure 3d, in which the deposited layer of substrate capable of absorbing X-ray and/or ultraviolet radiation has been etched;

15 Figure 3f is a side elevational view corresponding to the side elevational view of Figure 3d, in which the deposited layer of substrate capable of absorbing X-ray and/or ultraviolet radiation has been etched, and in which the substrate has been partially etched; and

20 Figure 4 is a micrograph of tantalum squares covered with platinum silicide on a glass substrate, in which thin layers of metal and silicon were alloyed using a focused electron beam, in which after removal of the platinum layer a halo-carbide plasma was used to etch the silicon and tantalum layers, and in which the platinum silicide squares acted as an etch mask.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is therefore directed toward a direct write lithography technique for producing structures of etch-resistant metal/semiconductor compound on various substrate materials, with achievable linewidths below 50 nm. The obtained etch-resistant metal/semiconductor compounds are extremely resistant to halo-carbide and Freon plasma etching, making them excellent etch masks. This technique is intended to be used as lithography process or for fabricating X-ray and/or ultraviolet lithography masks.

The present invention can also be used as a method for fabricating molds for nanoimprint lithography (see S.Y. Chou, P.R. Krauss *et al.*, *Journal of Vacuum Science and Technology*, B15, 2897 and S.Y. Chou, US Patent 5,772,905, June 1998). The fabrication of molds for this lithography technique requires an etch mask with both high resolution and excellent resistance to chemicals used for etching the mold material. For example, silicides formed by localized heating of metal and silicon layers by an electron-beam lithography system provide such an etch mask.

In the different figures of the appended drawings, the corresponding elements are identified by the same reference numerals.

Appended Figures 1a, 1b, 1c and 1d illustrate various steps of a preferred embodiment of the method according to the present invention, for fabricating a structure 3 of silicide on a silicon substrate 1. This method uses a controlled and focused electron beam 4 (Figure 1b)

to anneal the silicon substrate 1 and a layer or film of metal 2 deposited on the substrate 1.

More specifically, one of the preferred embodiments of the method according to the invention, for fabricating a silicide structure 3, formed for example of ultra-narrow lines of conductive silicide, onto the silicon substrate 1 can be summarized as follows:

Figure 1a: a layer of metal 2 capable of reacting with silicon to form silicide is deposited on the previously cleaned silicon substrate 1 using for example an electron beam evaporation technique or cool sputtering in a low vacuum chamber (see Figure 1a);

Figure 1b: the layer of metal 2 and the silicon substrate 1 are annealed by applying the focused electron beam 4 to the layer of metal 2 to locally heat the metal and silicon and cause diffusion of the metal and silicon in each other to form silicide. It has been demonstrated (M. Yasuda, H. Kawata, K. Murata, K. Hashimoto, Y. Hirai and N. Nomura, *J. Vac. Sci. Technol.*, **B12**, 1362 (1994)) that temperatures greater than 400 °C can be obtained with a focused electron beam, such as the one produced in a Scanning Electron Microscope (SEM). The electron beam is also displaced, for example under the control of a computer, to expose a desired pattern to be given to the silicide structure (see Figure 1b);

- Figure 1c: the area exposed to the focused electron beam has been transformed into a silicide structure 3 due to the above mentioned diffusion of the metal and silicon in each other; and
- 5 Figure 1d: the sample of Figure 1c is immersed into an acid solution that is able to etch the metal film 2 but not the silicide structure 3. Usually, an *aqua regia* solution ($\text{H}_2\text{O} : \text{HCl} : \text{HNO}_3 = 8 : 7 : 1$) is a proper acid to perform this task. After this wet etch, only the area (silicide structure) having been exposed to the electron beam
- 10 will remain on the substrate.

Exposure to the electron beam 4 may deposit some carbon at the surface of the silicide structure 3, which carbon may be removed through an oxygen plasma etch. During the evaporation process, the metal of the layer 2 may react at room temperature with the silicon of the substrate 1 to form a thin layer (not shown) of metal rich silicon. This undesirable layer can be removed by a wet etching of the silicon. A standard chemical etch such as $\text{H}_2\text{O} : \text{HNO}_3 : \text{HF} = 50 : 49 : 1$

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20 can be used for that purpose.

Another preferred embodiment of the method according to the invention may be summarized as follow:

25 Figures 3a, 3b, 3c, 3d, 3e and 3f illustrate a method for fabricating ultra small structures of a silicide and how to use these silicide structures as an etch mask. The technique uses a computer-controlled

focused electron beam to pattern the silicide structures on the surface of the substrate. This method comprises the following steps:

- 5 - Figure 3a: A layer of silicon 5 is deposited on the substrate 6, and
 a layer of metal 7 is then deposited on the layer of
 silicon 5. Deposition of the layers 5 and 7 is performed
 by either an electron beam evaporation technique, a
 thermal evaporation technique or by cool sputtering in
 a low vacuum chamber. Alternatively, the method can
10 also be done by inverting the order of deposition of the
 silicon and metal layers 5 and 7; more specifically, the
 layer of metal 7 is first deposited on the substrate 6
 and, then, the layer of silicon is deposited on the metal
 layer 7. This technique can be used on substrates of
 clean silicon, silicon carbide, glass, quartz, tantalum,
15 titanium, tungsten and any other substrate which resists
 the chemical etching of the top metal layer 7. The
 substrate 6 may comprise a deposited layer 8 or
 several deposited layers such as 8 of any of the above
 materials on the substrate 6 which can then be made of
20 any material.
- Figure 3b: The metal and silicon layers 5 and 7 are annealed using
 a focused electron beam 9. It has been shown that
 temperatures greater than 400° C can be obtained with
25 a focused electron beam, such as one found in a
 scanning electron microscope (SEM) [Yasuda, M.,
 Kawata, H., Murata, K., Hashimoto, K., Hirai, Y.,

5 Nomura, N., Journal of Vacuum Science and Technology, **B12**, 1362, (1994)]. The temperature to form the silicide of several metals varies from 200 - 700° C [Sze, S.M., Physics of Semiconductor Devices, 2nd edition, Willey, New York, (1990)]. In this method, the current density must be sufficiently high to reach the energy necessary to form the silicide. Silicide 10 is formed over the substrate 6 in the regions exposed to the electron beam 10 [Drouin, D., Beauvais, J., Lemire, R., Lavallée, E., Gauvin, R., Caron, M., Applied Physic Letters, **70**, 3020, (1997)]. The electron beam is controlled by a computer to form patterned structures of silicide 10.

15 Figure 3c: (a) The sample is immersed in an acid solution that is able to etch the top metal film 7, leaving the silicide structure 10 intact. Usually, an *aqua regia* solution ($H_2O : HCL : HNO_3$) is a proper acid to perform this task.

20 (b) Alternatively, a halo-carbide plasma is used to etch, i.e. remove the top silicon layer 5, leaving the silicide structure 10 intact.

Figure 3d: (a) An halo-carbide plasma is used to etch and remove the silicon layer 5.

25 (b) Alternatively, the sample is immersed in an acid solution that is able to etch the metal film 7, leaving the silicide structure 10 intact. Usually, an *aqua regia*

solution ($\text{H}_2\text{O} : \text{HCL} : \text{HNO}_3$) is a proper acid to perform this task.

After this etching operation, only the silicide structure 10 formed by the electron beam 9 remain over the substrate 6 or deposited layer 8.

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Figures 3e-f

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Etching of the remaining layer(s) 8 and eventually a portion of the substrate 6 under the layer(s) 8 is performed using either a directional plasma, a non-directional plasma or a wet etch. In any case, the silicide 10 acts as an etch mask, i.e. areas underneath the silicide structure 10 are not etched. In the case of wet etching and non-directional plasma etching however, a certain undercut may occur under the silicide structure 10 due to the non-directionality of the etch.

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The electron beam 9 may deposit some carbon at the surface of the silicide 10, this carbon may be removed by an oxygen plasma etch.

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Example 1

In this example, the method in accordance with the present invention will be applied to the production of a platinum silicide.

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The activation energy to first form Pt_2Si is around 1.4 eV and the temperature range is situated between 200-350 °C. The growth

of PtSi takes place only when all the Pt is transformed into Pt_2Si , the activation energy in this case is increased to 1.6 eV and the range of temperature formation is 300-450 °C (E.G. Colgan, *J. Mater Res.*, **10**, 1953 (1995)). Thus it is possible to form patterned platinum silicide structures, that is carrying out the method of the invention using a
5 standard SEM system.

Platinum layers of several thicknesses (20 nm to 100 nm) were evaporated onto clean n-type high resistivity silicon <100> substrates using an electron gun deposition system with an evaporation
10 rate of 0.5 nm/s. To carry out the present invention into practice, a electron beam lithography system consisting of a JEOL JSM-6300 Scanning Electron Microscope (SEM) equipped with a tungsten filament and a beam blander and controlled with the NPGS (Nanometer Pattern Generation System ver. 7.5, by J.C. Nability Lithography Systems)
15 lithography software. A SEM produces a highly focused electron beam suitable to produce sub-micron silicide structures. Exposures were carried out at several low energies (1 keV to 5 keV) and the unexposed platinum was removed from the silicon surface using an *aqua regia* solution of $\text{H}_2\text{O} : \text{HCl} : \text{HNO}_3 = 8 : 7 : 1$. An etch time of 4 minutes at
20 80°C was used. The difference in etch rates for the unexposed Pt and the silicide was sufficient to obtain a selective etch. However, prolonged etching can remove the silicide structure.

Figure 2a shows an Auger Electron Spectroscopy (AES)
25 depth profile of a 50 nm Pt thin film as deposited. As expected a smooth transition from the deposited layer to the substrate can be observed. In Figure 2b, the analysed sample consists of a 20µm x 20µm structure

exposed with the electron beam. The line dose used to produce the square was 17 $\mu\text{C}/\text{cm}$. The surface of the platinum silicide is contaminated with carbon which originates from the SEM chamber. A plateau can be observed corresponding to a Pt_2Si region. From this spectrum it is clear that the heating effect of the focused electron beam is sufficient to enable the diffusion of silicon through the metal layer (R. Pretorius, M.A.E. Wandt and J.E. McLeod, *J. Electrochem. Soc.*, **136**, 839 (1989)) and form platinum silicide which has a smaller etch rate than pure Pt. This difference in etch rates provides a means to pattern the metal layer with sub-micron resolution.

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The formation of the silicide depends on several factors. The thickness of the deposited layer determines the values of the accelerating voltage of the electron beam. Better results have been observed when the maximum dissipated energy of the electrons occurs in the metal layer near the junction with silicon. Another important factor that determines the temperature rise is the current density. Experiments have been carried out with a tungsten filament and the current density is approximately 100mA/cm² for a 1 keV electron beam (J.I. Goldstein, D.E. Newbury, P. Echlin, D.C. Joy, A.D. Romig Jr., C.E. Lyman, C. Fiori, E. Lifshin, *Scanning Electron Microscopy and X-Ray Microanalysis*, Second Edition, Plenum Press, New York, 1994, pp 820). This value decreases slightly for currents lower than 100 pA. Also, the current density increases with the electron beam energy, due to the smaller probe size. The higher the current density the higher is the heat obtained at the interface Pt-Si. The last parameter that determines the formation of the silicide is the electron beam exposure time or the line dose. A threshold line dose is

required to form the silicide; when the exposed time is lower than the threshold value, the pattern will not resist the wet etching.

Example 2

5 As an example to form fine structures using 20 nm of Pt evaporated on a silicon substrate, a 3 keV electron beam would be adequate. In fact, linewidths less than 50 nm have been obtained using a 100 pA electron beam ($\approx 200 \text{ mA/cm}^2$), $1.5 \text{ } \mu\text{C/cm}$ dose. In this case, to reduce the carbon contamination and the local charging effects, the
10 complete dose was achieved by multiple exposition (J. Fujita, H. Watanabe, Y. Ochiai, S. Manako, J.S. Tsai and S. Matsui, *Appl. Phys. Lett.*, **66**, 3065 (1995)). More specifically, each segment of the microstructure has been exposed 20 times using a reduced line dose of $0.075 \text{ } \mu\text{C/cm}$. The effect of carbon contamination is to absorb some of the
15 electron energy, thus reducing the amount of energy lost in the metal layer and decreasing the temperature rise. This technique of multiple exposition reduces the total line dose required for threshold, by reducing the rate of carbon deposition. Multiple repetition also significantly decreases the linewidth at threshold. For a given line dose, multiple
20 repetition implies a series of shorter exposure times for the pattern. In this case, the temperature required for silicide formation may only be attained in the center of the beam due to its Gaussian profile, thus creating the silicide in a region which is narrower than the beam diameter.

25 After the wet etch, the unexposed area may be contaminated with Pt. In fact, the first few nanometers of Pt evaporated can react with silicon at room temperature to form a silicide of about 2 nm

in thickness (L. Ley, Y. Wang, V. Nhuyen Van, S. Fisson, D. Soche, G. Vuye and J. Rivory, *Thin solids film*, **270**, 561 (1995)), thereby decreasing the surface resistivity of the silicon. The surface resistivity was restored to its original value by using a second wet etch conducted during 6 minutes in $\text{H}_2\text{O} : \text{HNO}_3 : \text{HF} = 50 : 49 : 1$. Also, to remove the surface carbon contamination due to prolonged beam exposure in the SEM chamber, the surface of the silicide structure can be exposed to an oxygen plasma etch for 20 minutes.

Proximity effects are reduced dramatically with the method according to the invention. In fact, with this method, proximity effects have been observed only within the range of the electron beam diameter. Accordingly, by using a high performance SEM, the beam diameter will be reduced and the current density will be increased. Finer structure with relatively insignificant proximity effects will then be achievable using an even smaller line dose.

A second important point to note is that no lift-off is required here as in the case of resist based processes. Such lift-off processes can significantly reduce resolution and reduce the yield.

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Example 3

The details of the method presented in this example will emphasize the particular case of fabrication of masks for X-ray and/or ultraviolet lithography using a platinum silicide. The activation energy to form the first type of platinum silicide (Pt_2Si) is around 1.4 eV and the temperature range for a complete transformation of Pt into Pt_5Si is from

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200 - 350° C [Colgan, E.G., Journal of Material Resistance, 10, 1953, (1995)]. A focused electron beam of a standard scanning electron microscope (SEM) at low energy (1 to 3 keV) provides sufficient energy to locally form this silicide, despite the heat dissipation in the material.

5 A tantalum layer of 450 nm was evaporated onto a substrate of clean material transparent to X-ray and/or ultraviolet radiation (for example glass) or reflective to ultraviolet radiation (for example a substrate used for the fabrication of ultraviolet masks consists of a series of thin layers of molybdenum in between layers of silicon), using an
10 electron gun deposition system. For X-ray lithography, the material opaque to X-ray radiation can be tantalum, tungsten, tantalum silicide, and tungsten silicide. For ultraviolet lithography, tantalum, tantalum silicide, titanium, chromium, and nickel silicide can be used as material opaque to ultraviolet radiation. Using the same deposition system, a 40
15 nm layer of silicon is deposited on the tantalum layer and a 20 nm layer of platinum is deposited on the layer of silicon. Alternatively, the layer of platinum can be deposited on the layer of tantalum and the layer of silicon on the layer of platinum. The electron beam lithography system consists of a JEOL JSM-6300 scanning electron microscope (SEM) equipped with
20 a tungsten filament and a beam blanker, controlled by the NPGS [Nanometer Pattern Generation System, version 7.6, by J.C. Nability Lithography Systems] lithography software. Exposures were carried out at 1.4 keV.

25 The unexposed platinum was removed from the silicon surface using a dilute aqua regia solution of $\text{H}_2\text{O} : \text{HCL} : \text{HNO}_3 = 8 : 7 : 1$

at 80° C. An etch time of 1 minute was used. Under these conditions, the silicide is left intact by the wet etch.

A $\text{CF}_4 : \text{O}_2$ plasma is then used to remove the silicon layer and the tantalum layer. Silicide structures act as an etch mask, being unaffected by the plasma etching. Regions underneath the silicide structures are therefore protected and left intact. Although this was performed in the present case using a non-directional plasma etch, similar results could be achieved using a directional plasma etching system, such as a reactive ion etcher (RIE). In our case, sidewalls are not perpendicular to the surface, due to the non-directionality of the plasma etch. A reactive ion etching or other non-isotropic etch system could achieve perpendicular sidewalls, therefore a greater resolution. Figure 4 shows an example of a structure obtained with this method, after the final plasma etch.

With this method, both the resolution and the chemical resistance of the fabricated silicide structures are sufficient to meet the industrial requirements for fabricating masks for X-ray and/or ultraviolet lithography. Platinum silicide has an excellent resistance to many chemical etches, especially to the halo-carbide plasmas used to etch the tantalum layer. In this case, tantalum was chosen for its excellent mechanical properties and good chemical resistance, which are needed for the periodical cleaning of masks used in industry. Tantalum also has a high atomic number that makes it a good X-ray and ultraviolet radiation absorbent.

Example 4

Another example of the method is the fabrication of molds for nanoimprint lithography. These molds need to be resistant to mechanical constraints that are applied to transfer the pattern from the mold to a mechanically incompressible surface. The fabrication of molds requires an etch mask which has both high resolution and excellent resistance to the chemicals used to etch the mold substrate. With our technique, a mechanically resistant substrate (such as tantalum or silicon carbide) is covered by a thin layer of silicon, followed by a thin layer of a metal able to form silicide. Alternatively, the thin layer of metal can be deposited on the substrate and the thin layer of silicon deposited on the thin layer of metal. The electron beam lithography system transfers the pattern by forming silicide regions on the surface. Wet etching in a strong acid is used to remove the thin metal layer in unexposed regions. Similarly, a plasma etch or a wet etch can be used to remove the thin silicon layer in unexposed regions. A reactive ion etcher or any directional etching process can then be used to etch the substrate. Exposed regions of the substrate are covered by silicide and are therefore protected, while grooves are etched elsewhere, thus creating a mold that can be used in nanoimprint lithography.

Example 5

A last example of the method is the fabrication of MOS (metal-oxide-semiconductor) structures. A 50 nm silicate (SiO_2) layer is deposited using a plasma enhanced chemical vapor deposition system (PECVD) on a clean silicon substrate. 20 nm layers of platinum and silicon are then evaporated using an electron gun deposition system, silicon on top. Lithography is performed using the same SEM and

software as in the previous example. The thin silicon layer on top is removed by a $\text{CF}_4 : \text{O}_2$ plasma. Afterward, the platinum layer is removed using a dilute aqua regia solution of $\text{H}_2\text{O} : \text{HCL} : \text{HNQ} = 8 : 7 : 1$ at 80°C . Both etches do not attack the silicide structures formed by the electron beam. The silicide structures are then used as an etch mask during the $\text{CF}_4 : \text{O}_2$ plasma etch of the quartz layer. The silicate layer is completely removed except for the regions underneath the silicide structures.

In summary, a novel fabrication method to produce sub-50 nm metallic lines for use as thin conducting structures or even as etching masks on a vast variety of substrates has been disclosed. This method should reduce the proximity effects present in resist-based lithography and provide a resolution limit superior to the 50 nm linewidth obtained using a tungsten filament SEM. Also, the method is suitable for the fabrication of masks for X-ray and/or ultraviolet radiation lithography that meet the requirements of industry in terms of material resistance and resolution, and for the fabrication of molds for nano-imprint lithography and for the fabrication of MOS structures.

Although the present invention has been described hereinabove with reference to preferred embodiments thereof, these embodiments can be modified at will, within the scope of the appended claims, without departing from the spirit and nature of the subject invention. As non limitative examples:

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- semiconductor materials, other than silicon (Si), such as gallium arsenide (GaAs) could be used;

- with a substrate of silicon (Si), the metal can be selected from the group consisting of: cobalt (Co), chrome (Cr), hafnium (Hf), iridium (Ir), manganese (Mn), nickel (Ni), palladium (Pd), platinum (Pt), rhodium (Rh), tantalum (Ta), titanium (Ti), tungsten (W), zirconium (Zr), copper (Cu) and silver (Ag); and

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- with a substrate of gallium arsenide (GaAs), at least platinum (Pt) could be used as metal.



WHAT IS CLAIMED IS:

1. A method for fabricating a mask for X-ray and/or ultraviolet lithography, comprising:
 - 5 providing a substrate made of material transparent to X-ray and/or ultraviolet radiation or reflective to ultraviolet radiation;
 - depositing on the substrate a layer made of material opaque to X-ray and/or ultraviolet radiation;
 - depositing on the layer of material opaque to X-ray and/or ultraviolet radiation two superposed layers, said two superposed layers comprising a layer of semiconductor material and a layer of metal capable of reacting with the semiconductor material to form an etch-resistant metal/semiconductor compound;
 - 10 producing a focused electron beam;
 - 15 applying the focused electron beam to the superposed layers of metal and semiconductor material to locally heat the metal and the semiconductor material and cause diffusion of metal and semiconductor material in each other to form etch-resistant metal/semiconductor compound;
 - 20 displacing the focused electron beam on the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound; and
 - etching the layer of metal, the layer of semiconductor material and the layer of material opaque to X-ray and/or ultraviolet



radiation to leave on the substrate the structure of etch-resistant metal/semiconductor compound and the layer of material opaque to X-ray and/or ultraviolet radiation underneath the structure of etch-resistant metal/semiconductor compound to thereby form said mask for X-ray and/or ultraviolet lithography.

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2. A method for fabricating a mask as defined in claim 1, wherein depositing the two superposed layers comprises:

depositing the layer of semiconductor material on the layer of material opaque to X-ray and/or ultraviolet radiation; and

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depositing the layer of metal on the layer of semiconductor material.

3. A method for fabricating a mask as defined in claim 1, wherein depositing the two superposed layers comprises:

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depositing the layer of metal on the layer of material opaque to X-ray and/or ultraviolet radiation; and

depositing the layer of semiconductor material on the layer of metal.

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4. A method for fabricating a mask as defined in claim 1, wherein the material transparent to X-ray and/or ultraviolet radiation comprises glass, silicon nitride, silicon carbide, silicon dioxide, and diamond film.



5. A method for fabricating a mask as defined in claim 1, wherein the material opaque to X-ray and/or ultraviolet radiation is selected from the group consisting of: tantalum, tantalum silicide, tungsten, tungsten silicide, titanium, chromium, nickel silicide, TaB₄, WB₄, chromium silicide, and nickel.

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6. A method for fabricating a mask as defined in claim 1, wherein the mask is a mask for X-ray lithography and wherein the material opaque to X-ray radiation is selected from the group consisting of: tantalum, tantalum silicide, tungsten, tungsten silicide, TaB₄ and WB₄.

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7. A method for fabricating a mask as defined in claim 1, wherein the mask is a mask for ultraviolet lithography and wherein the material opaque to ultraviolet radiation is selected from the group consisting of: tantalum, tantalum silicide, titanium, chromium, nickel silicide, chromium silicide and nickel.

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8. A method for fabricating a mask as defined in claim 1, wherein the semiconductor material comprises silicon and wherein the metal is selected from the group consisting of cobalt, chromium, hafnium, iridium, manganese, nickel, palladium, platinum, rhodium, tantalum, titanium, tungsten, zirconium, copper and silver.

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9. A method of fabricating a mask as defined in claim 1, wherein:



producing a focused electron beam comprises producing a highly focused electron beam; and

displacing the focused electron beam comprises displacing the highly focused electron beam on the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound.

10. A method of fabricating a mask as defined in claim 1, wherein displacing the focused electron beam on the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound comprises exposing each portion of the structure of etch-resistant metal/semiconductor compound to the focused electron beam once or a plurality of times.

11. A method of fabricating a mask as defined in claim 1, wherein:

the material transparent to X-ray and/or ultraviolet radiation comprises glass;

the material opaque to X-ray and/or ultraviolet radiation comprises tantalum;

the semiconductor material comprises silicon;

the metal capable of reacting with the semiconductor material to form an etch-resistant metal/semiconductor compound comprises platinum;



the etch-resistant metal/semiconductor compound comprises platinum silicide.

12. A method for fabricating a mask as recited in claim 11, wherein etching the layer of platinum, the layer of silicon, and the layer of tantalum comprises:

wet etching the platinum layer; and
plasma etching both the silicon and tantalum layers.

13. A method for fabricating a mold for imprint lithography, comprising:

providing a mechanically resistant substrate;
depositing on the substrate two superposed layers, said two superposed layers comprising a layer of semiconductor material and a layer of metal capable of reacting with the semiconductor material to form etch-resistant metal/semiconductor compound;

producing a focused electron beam;
applying the focused electron beam to the superposed layers of metal and semiconductor material to locally heat said metal and semiconductor material and cause diffusion of said metal and semiconductor material in each other to form etch-resistant metal/semiconductor compound;

displacing the focused electron beam onto the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound; and



etching the layers of metal and semiconductor material to leave on the substrate only the structure of etch-resistant metal/semiconductor compound, wherein said structure or etch-resistant metal /semiconductor compound forms an imprint of said mold and wherein said structure and substrate form said mold for imprint lithography.

14. A method for fabricating a mold as defined in claim 13, wherein depositing the two superposed layers comprises:

depositing the layer of semiconductor material on the substrate; and

depositing the layer of metal on the layer of semiconductor material.

15. A method for fabricating a mold as defined in claim 13, wherein depositing the two superposed layers comprises:

depositing the layer of metal on the substrate; and
depositing the layer of semiconductor material on the layer of metal.

16. A method for fabricating a mold as defined in claim 13, wherein the substrate is made of a material selected from the group consisting of: clean silicon, silicon carbide, glass, quartz, tantalum, titanium, tungsten, tantalum silicide, tungsten silicide, TaB₄ and WB₄.



17. A method for fabricating a mold as defined in claim 13, wherein the semiconductor material comprises silicon and wherein the metal is selected from the group consisting of cobalt, chromium, hafnium, iridium, manganese, nickel, palladium, platinum, rhodium, tantalum, titanium, tungsten, zirconium, copper and silver.

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18. A method of fabricating a mold as defined in claim 13, wherein:

producing a focused electron beam comprises producing a highly focused electron beam; and

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displacing the focused electron beam comprises displacing the highly focused electron beam on the superposed layers of metal and semiconductor material to form a sub-micron structure of etch-resistant metal/semiconductor compound.

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19. A method of fabricating a mold as defined in claim 17, wherein displacing the focused electron beam on the superposed layers of metal and semiconductor material to form a structure of etch-resistant metal/semiconductor compound comprises exposing each portion of the structure of etch-resistant metal/semiconductor compound

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to the focused electron beam once or a plurality of times.