I. INTRODUCTION

In electron-beam lithography, several limitations come from the electron-sensitive resists. The most significant are the limitations in resolution due to the polymeric or organic nature of resists, the proximity effects when exposing closely spaced structures, and the poor resistance to chemical etchants used in microelectronics. One of these techniques, the silicide direct-write electron-beam lithography process (SiDWEL) was developed to take advantage of the excellent resistance of some silicides to chemical etchants used in microelectronics. In this process, a thin metallic film such as Cr, Cu, Ni, Pt, or Pd, typically of 20 nm, is deposited on a silicon substrate or a silicon layer. A low-energy electron-beam lithography system is then used to enable intermixing at the metal–silicon interface. Energies used are usually between 1 and 3 keV. In these conditions, all the energy is lost near the metal–silicon interface, enabling the formation of silicide at the interface. After exposure, a wet etching is performed on the sample to remove the unexposed metal regions. Thermal effects are then used to remove the unexposed metal regions. Thermal calculations are performed using a Monte Carlo simulation of electron trajectories and are correlated with experiments using Ni as the thin metallic film. A comparison of the doses required for the formation of several metals is also done. Results show that the SiDWEL process is possible when the electrons lose all their energy in a layer thickness comparable to the phonon mean free path. Finally, experiments are performed using multilayer samples to form silicide structures.

This article presents elements of a simple model for the simulation of the SiDWEL process, by using a Monte Carlo simulation to calculate the average depth of penetration of the electrons in the metal and silicon layers. Classical thermodynamics is then used to describe energy propagation. The model takes into account that part of the energy which is absorbed at the metal–semiconductor interface for the intermixing of the layers. The effect of the metallic layer density is discussed for different metals. Afterwards, a threshold dose is fitted to experiment and a comparison is made with experimental data as a function of the thickness of the metal layer for nickel silicide. In another experiment, multilayer samples are used to demonstrate heat diffusion and its impact on the resolution of the process. The proposed model provides a better understanding of the silicide formation mechanisms in the SiDWEL process.

II. PROCESS SIMULATION AND MODEL

As a basis of the model, each electron is treated individually. A Monte Carlo simulation is performed to determine the average depth of penetration of electrons into the metal thin film. Table I gives this average depth of penetration for different metals for electrons at 1.4 keV. In most of the studied cases, the electron average depth of penetration is less than 10 nm. The dissipation of heat is calculated using the equation

$$\frac{\partial H(x,y,z,t)}{\partial t} + D \nabla^2 H(x,y,z,t) = S(x,y,z,t),$$

\[ S = 0 \quad \text{for} \quad (t > 0), \]

\[ S = S_0 \quad \text{for} \quad (t = 0 \quad \text{and} \quad x,y,z < p). \]
TABLE I. Average depth of penetration and threshold dose for different metals. No silicide structures were formed with Al, Au, and Ti.

<table>
<thead>
<tr>
<th>Depth of penetration (nm)</th>
<th>Threshold dose (mC/cm²)</th>
<th>Etch solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>9</td>
<td>19 CrO₃:H₂O+-(NH₄)₂Ce(NO₃)₆</td>
</tr>
<tr>
<td>Cu</td>
<td>9</td>
<td>9 HNO₃:H₂O</td>
</tr>
<tr>
<td>Ni</td>
<td>8</td>
<td>28 HNO₃.CH₂CHOHCH₂.H₂O</td>
</tr>
<tr>
<td>Ni</td>
<td>8</td>
<td>&gt;100 HNO₃:HCl₂H₂O</td>
</tr>
<tr>
<td>Pd</td>
<td>7</td>
<td>56 HNO₃:HCl₂H₂O</td>
</tr>
<tr>
<td>Pt</td>
<td>6</td>
<td>74 HNO₃:HCl₂H₂O</td>
</tr>
<tr>
<td>Al</td>
<td>24</td>
<td>n/a HCl:HI₄F</td>
</tr>
<tr>
<td>Au</td>
<td>7</td>
<td>n/a HNO₃:HCl₂H₂O</td>
</tr>
<tr>
<td>Ti</td>
<td>15</td>
<td>n/a HCl:HI₄F</td>
</tr>
</tbody>
</table>

where \( H \) is the heat in the sample, \( D \) the thermal diffusion constant, \( S \) the heat source, and \( p \) the depth of penetration. \( S_0 \) corresponds to the energy of the electron. A cubic integration unit with side dimensions equal to \( p \) is used to numerically solve Eq. (1). It is necessary for the validity of this approximation to have an electron average depth of penetration \( p \) in the order of the phonon mean free path \( l_p \). This can be verified using the Leibfried and Schlömann approximation

\[
l_p = \frac{20}{\gamma} \frac{T_M}{T} a,
\]

where \( T \) is the sample temperature, \( T_M \) the melting temperature of the material, \( a \) the lattice constant, and \( \gamma \) the Grüneisen constant of the material. For each metal investigated, the mean free path was of the order of 5 nm, smaller than the average depth of penetration given in Table I. For situations with \( p \gg l_p \), the cubic integration unit approximation used for solving Eq. (1) is no longer valid, while for situations with \( p < l_p \), the use of the average electron depth of penetration to determine the size of the heat source \( S_0 \) is not a valid approximation.

In solving the heat diffusion equation [Eq. (1)], the thermal diffusion constant \( D \) is approximated to be the same for the whole sample. During calculation of the thermal diffusion, the amount of heat flowing through the surface is summed. In the model, part of this heat energy is absorbed at the metal–silicon interface to form the silicide since the activation energy for the formation of some silicides is very low, approximately of 1 eV. Although the proportion of energy absorbed at the interface cannot be determined by this model, a threshold of the summed energy flowing through the metal–silicon interface is set based upon experimental measurements. For all the results presented below, the threshold was determined using experimental values for 1.4 keV electrons and a 20 nm thick nickel thin film. The model approximates a flat random distribution of electrons in the beam diameter. Energy being dissipated isotropically in the material, a geometrical factor \( (t^2/p^3) \), where \( t \) is the metal layer thickness, is used to take into account the area of the region at the metal–silicon interface heated by each electron.

III. EXPERIMENTAL METHOD

Experiments are conducted on silicon substrates. Samples are cleaned using trichloroethylene, acetone, and 2-propanol; an etch in a hydrofluoric acid solution is then performed to remove the native oxide layer. The metal layers are deposited using an electron gun evaporator. Lithography is conducted with a JEOL-6300 tungsten filament scanning electron microscope, externally controlled by lithography software. The exposed pattern consists of an array of lines, 10 μm long and of widths ranging from 3 μm down to 100 nm. The electron beam current used was 100 pA. At an energy of 1.4 keV, with this beam current, the electron beam diameter is measured to be approximately 320 nm; at 1.0 keV, it is approximately 360 nm and at 3.0 keV, it is approximately 250 nm. After exposure, a wet etching acid solution is used to remove unreacted metal, the solution used being chosen according to the metal to etch. In order to allow comparisons between different metals, the various acid solutions were adjusted by water dilution such that a time of 45–60 s is required to etch the 20 nm metal layers. In each case, 15 s were added to the etch time to insure a complete removal of unreacted metal. The condition for setting the threshold dose is continuity of the narrowest lines (100 nm wide). The feasibility of structures smaller than the beam diameter can be explained by the Gaussian-shaped beam. Only the central part of the beam has a current density sufficient to achieve silicide formation at the threshold dose. In typical experiments, the same pattern is repeated with increasing doses, in a range from 5 to 500 mC/cm². To determine the threshold dose for different metals, each experiment is repeated at least three times and the least value is taken as the threshold. The 30% experimental uncertainties correspond to steps in the dose range.

IV. RESULTS AND DISCUSSION

A. Metal density

Line array patterns where exposed at 1.4 keV on 20 nm layers of different metals. Table I gives the threshold dose, the etch solution used, and the average calculated depth of penetration for Cr, Cu, Ni, Pd, and Pt. The SiDWEL process did not work with the Au, Ti, and Al layers. In the first case, it is well known that it is very difficult to form an Au silicide by annealing, due to the chemical stability of gold. Monte Carlo simulations conducted with Ti and Al demonstrate that at 1.4 keV, the average depth of penetration of the electrons in the metal layer is greater than 15 nm, while for the other metals (Cr, Cu, Ni, Pd, and Pt), the depth of penetration is smaller than 10 nm. This is mainly due to the metal density, Al and Ti having densities of 2.3 and 4.5 g/cm³, respectively, compared to densities over 7 g/cm³ for all the other tested metals. Since energy is dissipated in a larger volume, less energy per surface flows through the metal–silicon interface than for metal with higher metal density. The average depth of penetration of electrons being more than twice the phonon mean free path, it is not possible to perform calculations of heat dissipation with this model for Al and Ti.
As seen in Table I, among the metals forming silicide by the SiDWEL process, copper has the lowest threshold dose. It is nevertheless difficult to completely etch away the unexposed Cu thin film since regions of very shallow silicide form during the evaporation of the metal layer. Platinum requires the highest threshold doses, followed by palladium. Although the etch time for each solution being used in this study is comparable, it is not possible to evaluate the chemical selectivity between the metal regions and the silicide structures for the different solutions. However, experiments conducted using a nickel thin film with different etch solutions demonstrate that much of the variation of threshold dose is solution dependent. In general, doses for the SiDWEL process are much higher than for the standard resist process, but the SiDWEL lithography process is dependent on the beam current density. With high current density, a significant temperature rise occurs at the metal–silicon interface, allowing lower threshold doses by an increase flow of energy at the interface.

B. Metal thickness

Figure 1 shows model predictions and experimental values of the threshold dose for nickel silicide obtained using a beam energy of 1.4 keV. Considering experimental uncertainties, the model is in good agreement with the measured values. An increase in the threshold dose as a function of the thickness is observed. This can be explained by the isotropic diffusion of heat in the metal layer, in accordance with Eq. (1). The shoulder visible on the calculated curve near a 40 nm thickness can be attributed to the geometrical factor. This factor limits the increase of the threshold dose for thicker layers to take into account the effects of electrons losing energy in close proximity to each other.

By using the same fitted parameter as for the 1.4 keV case, Fig. 2 shows a comparison of experimental values and curves from the proposed model at 1.0 and 2.0 keV. At 1.0 keV, the model is in agreement with the measured values, except for the 10 nm metal layer where the model underestimates the threshold dose. A shoulder is also present on the 1.0 keV curve around 25 nm which could correspond to flattening of the measured threshold dose above this thickness. At 2.0 keV, the model is in good agreement with measured values. Due to the increase of the average depth of penetration at this energy, the model makes no prediction for nickel layers thinner than 20 nm. A linear extrapolation of the curve, however, would overestimate the threshold dose for the 7 and 10 nm layers. This can be partly attributed to the depth of penetration of electrons at this energy (13 nm), which is significantly larger than the phonon mean free path found using Eq. (2). Another cause of error may be the limited accuracy of the Monte Carlo simulation at low energy.

C. Multilayer samples

In a different experiment, a stack of layers, Ni/Si/Ni/Si/Ni/Si/Ni, with each layer 10 nm thick, is deposited on a clean silicon surface by electron gun evaporation. The SiDWEL process is used with energies of 1.4 and 2.8 keV to form silicide patterns. First, a HNO3:CH3CHOHCH2:H2O etch solution is used to remove the unreacted top layer of Ni. Threshold doses are observed using the same criteria as for previous experiments. For both energies, the threshold is determined to be 19 mC/cm2. A diluted wet etching solution of HF:H2O2 is then used to remove all remaining layers in the unexposed regions. After this second etch, threshold doses are 74 mC/cm2 for 1.4 keV and >100 mC/cm2 for 2.8 keV. This is in agreement with previous simulations and experiments on nickel layers, demonstrating that for layer thicknesses >40 nm the threshold dose increases with energy.

Figure 3 shows a micrograph of a silicide structure from a multilayer sample exposed at 1.4 keV, with a 74 mC/cm2 dose. The first four layers are visible in the slope of the structure. The remaining three layers of the stack are underneath and are not individually distinguishable on the micrograph. The presence of the stripes for the four superior layers indicates that they are probably only partially alloyed. The slope at the edge of the structure is in agreement with the model which in such a situation predicts a widening of the silicide structures as a function of the depth in the material due to the isotropic diffusion of heat. For nanofabrication purposes, this demonstrates that resolution is limited by the thickness of the metal layer.
V. CONCLUSION

The SiDWEL process was demonstrated with Cr, Cu, Ni, Pd, and Pt, while for lower density metals, Al and Ti, no silicide were formed. The smallest threshold doses have been attained with copper silicide. A model is presented that calculates the energy flowing through the metal–silicon interface using classical thermal diffusion for single electrons. The model approximates the electron beam as a random distribution of electrons. Experiments conducted on nickel silicide to find the threshold dose of the SiDWEL process as a function of the metal layer thickness are in good agreement with the presented model for energies lower than 2 keV. Discrepancies between the model and experiments are due to approximations in the heat dissipation calculations and to limitations of the Monte Carlo simulation. Other experiments were conducted on multilayer samples at 1.4 and 2.8 keV. These demonstrate that the maximum achievable resolution for the process is limited by the metal layer thickness and by the electron beam diameter. With a field emission gun electron source, it would be possible to reduce the beam diameter and to increase the current density, thus lowering the threshold doses for this process. The SiDWEL process could then be used directly for the fabrication of transistors arrays, and also as an etch mask for the fabrication of nanostructures, with significant advantages over conventional resists.

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