Rare Earth Metal Silicides Synthesized by High Current Metal Ion Implantation

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Abstract. The YSi2, LaSi2, CeSi2, PrSi2, NdSi2, SmSi2, GdSi2, TbSi2, DySi2, and ErSi2 layers were formed on Si wafers by respective high current metal-ion implantation using a metal vacuum vapor arc (MEVVA) ion source and the formation temperature was considerably lower than the critical temperatures (300-350°C) required for the rare earth metal silicides by solid-state reaction. It was found that the crystalline structures could be improved with increasing slightly the formation temperature as well as the implantation dose. Concerning the growth kinetics, in some cases, fractal patterns were observed on Si surfaces and the branches of the fractals consisted of the grains of respective precipitated silicides. Interestingly, the fractal dimension increased with formation temperature and eventually approached to a value of 2.0, corresponding to a continuous layer, which was required in practical application. The formation mechanism as well as the growth kinetics was discussed in terms of the far-from-equilibrium process involved in the MEVVA ion implantation.

INTRODUCTION

Over the last few decades, the development of sub-micron devices on silicon wafers has gained considerable attention as well as great success in the semiconductor integrated circuit technology. In particular, the high quality metal silicides have attracted increasing interest in regard to their practical application as contacts at the source/drain regions of the future Si MOSFET and interconnect metallization materials in electrical devices because of their low electrical resistance, good uniformity, high chemical and thermal stability [1-3]. In recent decades, rare earth (RE) metal silicides have also attracted much attention because of their unique electrical conduction. For instance, the RE metal silicides frequently feature the lowest Schottky barrier height on n-type silicon [4]. These properties make RE metal silicides excellent candidate materials in fabrication of the infrared detectors. Consequently, various techniques have been developed to synthesize RE metal silicides, such as solid-state reaction (SSR) and ion beam synthesis (IBS) using conventional implanters.

To form the RE metal silicide, a scheme named SSR between deposited metal layer/Si substrate, has been employed. In practice, in-situ heating under ultra high vacuum was recommended because the RE metals are extremely reactive. It was found that the interaction between RE metals and single crystalline silicon frequently exhibited a critical temperature phenomenon [5-7]. Below the critical annealing temperature, the interaction was very sluggish. Above the critical annealing temperature, the interaction was explosive and cannot be well controlled. Besides, high temperature annealing is also required and it, in turn, would be detrimental to the physical properties [8]. In order to control the interaction, the use of an energetic ion beam to trigger the reaction between the RE metal and silicon was developed, e.g., laser, electron, ion beam were used to induce the reaction. In IBS using the conventional implanter, the formation process consists of a first step of ion implantation to high dose at temperature range of 350-450°C and a second step of post-annealing conducted at a temperature as high as 1000°C [9]. A necessary implantation dose is on the order of $10^{17}$ ion/cm$^2$ and it typically requires several hours of irradiation using the conventional implanters to synthesize the metal silicides.

In the mid-1980s, a new ion source, namely the metal vapor vacuum arc (MEVVA) ion source, was invented [10], and it was capable of providing almost all the metal ion species with a very high current density up to greater than 100 µA/cm$^2$. Naturally, high current metal ion implantation into Si wafers to a dose of the order of $10^{17}-10^{18}$ ion/cm$^2$ could be very efficiently completed within about an hour and cause a significant temperature rise, e.g. up to 400-500°C, resulting in a simultaneous thermal annealing of the Si substrate, which could be benefit to the formation of the desired metal silicides. The authors’ group has employed the MEVVA ion source to synthesize some important metal silicides, such as C54-TiSi2 and β-FeSi2 [11,12]. The new scheme developed by the...
authors’ group was named as metal silicidation technique by high current metal-ion implantation using MEVVA ion source.

We present, in this paper, a brief summary of our recent results concerning the synthesis of a series of RE metal silicide layers on Si wafers by high current RE metal ion implantation, including the experimental observations of the formation of the RE metal silicide layers and the fractal pattern evolution during the growth of some RE metal silicides. In addition, the formation mechanism is also discussed for a better understanding concerning the energetically high current metal ion implantation process using the MEVVA ion source.

**EXPERIMENTAL PROCEDURE**

The MEVVA ion source used in this study can provide a metal ion beam with a current density up to 160 µA/cm² on a 12 cm diameter steel target holder at an extraction voltage of 50 kV. Because the implantation system has no analysis magnet, the extracted RE metallic ions were multi-charged states, which were determined by the time-of-flight method and their reproducibility was better than 90% as shown in Table 1. In calculating the ion range and range straggling, an average charge state of the ions was used according to their weight distribution [13]. Since the cathode of the MEVVA ion source is made of the RE metals with a purity of 99.99 wt%, the purity of the extracted ion beam is also considered to be at a similar level. The MEVVA ion implantation system has a base vacuum level of 2×10⁻⁴ Pa. Auger electron spectroscopy has been employed to measure the composition of the formed silicides and the results showed that the carbon content was less than 2% and the oxygen level was far less than that of carbon, which, in fact, was within the minimum scale of the instrument.

The silicon wafers used in this study were Si (111) and Si (100) with the resistivities of 8-10 and 20-50 Ω cm, respectively. The wafers were cut into 1×1 cm² samples, cleaned by a standard chemical procedure and then dipped in a dilute HF solution, followed by a rinse in deionized water. The cleaned samples were immediately loaded onto a steel-made sample holder in the target chamber of the MEVVA implanter operated at an extract voltage of 40 kV. During implantation, no deliberately heating or cooling was employed for the samples. RE metal ion species of Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, and Er were implanted into the Si wafers, respectively. The ion current densities varied from 8.8 to 35.2 µA/cm² and the implantation dose was ranged from 5×10¹⁶ to 4×10¹⁷ ions/cm². A thermal couple placed at the back of the wafers was used to measure the real temperature rise of the substrates during implantation, and the measuring error was about ±10°C. X-ray diffraction (XRD) was performed to identify the structure of the formed RE metal silicides after high current MEVVA ion implantation by a D/max-RB diffractometer operated with a Cu radiation of wavelength 1.54 Å at 40 kV and 120 mA. Rutherford backscattering spectrometry (RBS) was employed to measure the depth profiles of the implanted layer with 2.0 MeV He ions at a 165° scattering angle. A scanning electron microscope (SEM-6301F) was employed to examine the surface and cross sectional morphology of the Si wafers under various implantation conditions. Besides, an image-processing computer was used to calculate the fractal dimensions for the fractal patterns on the Si surface.

**RESULTS AND DISCUSSION**

The MEVVA ion implantation technique has some unique characteristics to synthesize the silicide layers at a designated formation temperature. Firstly, high current metal ion implantation into the Si wafers can cause a significant temperature rise as shown in Table 2, resulting in a simultaneous thermal annealing of the Si substrate. Since the metal ions from the MEVVA ion source are extracted in a pulse mode, its increase is actually achieved by increasing the pulse number within a unit time. Secondly, the ion current density and ion dose can readily be adjusted, i.e. it is very easy to obtain a controllable temperature, enabling one to trace the interaction of the metal and Si substrate in synthesizing the RE metal silicide step-by-step. Thirdly, the metal ions were dynamically launched into the Si lattice in a way of far-from-equilibrium, which is sharply different from that involved in SSR, where thermal diffusion and reaction played a predominant role. Because of the above characteristics, the formation temperature of RE metal silicides by high current MEVVA ion implantation could probably

<table>
<thead>
<tr>
<th>Ion species</th>
<th>Radio of the charge state (%)</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>5 62 33</td>
<td>2.3</td>
</tr>
<tr>
<td>La</td>
<td>1 76 23</td>
<td>2.2</td>
</tr>
<tr>
<td>Ce</td>
<td>3 83 14</td>
<td>2.1</td>
</tr>
<tr>
<td>Pr</td>
<td>3 69 28</td>
<td>2.2</td>
</tr>
<tr>
<td>Nd</td>
<td>3 83 17</td>
<td>2.2</td>
</tr>
<tr>
<td>Sm</td>
<td>2 83 15</td>
<td>2.1</td>
</tr>
<tr>
<td>Gd</td>
<td>2 76 22</td>
<td>2.2</td>
</tr>
<tr>
<td>Tb</td>
<td>2 85 13</td>
<td>2.1</td>
</tr>
<tr>
<td>Dy</td>
<td>2 66 32</td>
<td>2.3</td>
</tr>
<tr>
<td>Er</td>
<td>1 63 35 1</td>
<td>2.3</td>
</tr>
</tbody>
</table>
be considerably lower than that required in SSR. Furthermore, the MEVVA synthesizing RE metal silicides could be of a single-step process requiring neither in-situ heating, nor post-annealing.

**Structural Evolution**

We now present the experimental results of the structural evolution on the Si surface upon high current RE metal ion implantation using the MEVVA ion source. The XRD patterns confirmed the corresponding phases of the RE metal silicides under appropriate implantation conditions. Firstly, the RE metal silicide phases could be formed at the lowest ion current density conducted in this study, although the diffraction peaks of silicide phases were relatively weak in the XRD patterns. With increasing the ion current density, the crystalline structure of the phases obviously improved, as the intensities of all of the diffraction peaks increased, which suggested that increasing the temperature rise could directly improve the structural quality of the silicide phases. When the ion current density was increased to the highest value in this study, however, the structure of the corresponding phases improved only a little, because the time for RE metal/Si interaction at the high current density to a same implantation dose decreased. A specific system, i.e. the Nd-Si system, was selected for a detailed study to examine the structural evolution of the formed RE silicide with increasing the ion current density. One sees from Fig. 1(a) at a current density of 8.8 \( \mu \text{A/cm}^2 \), i.e., at a formation temperature of 165°C, almost all the diffraction peaks of the NdSi\(_2\) phase appear, indicating the NdSi\(_2\) phase can be formed at that temperature. It can be seen from Fig. 1(b), when the formation temperature was increased to 235°C, i.e.,

![Fig. 1. XRD patterns of Si (100) wafers implanted by Nd-ion with various current densities to a fixed dose of 1×10\(^{17}\) ions/cm\(^2\). (a) 8.8, (b) 17.6, and (c) 35.2 \( \mu \text{A/cm}^2 \).](image)

**TABLE 2. RE metal silicides synthesized by high current RE metal ion implantation into the Si Substrate and temperature rise.**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Current density (( \mu \text{A/cm}^2 ))</th>
<th>Nominal dose (ions/cm(^2))</th>
<th>Temperature rise (°C)</th>
<th>Silicide structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>8.8-35.2</td>
<td>0.5-2×10(^{17})</td>
<td>165-335</td>
<td>YSi(_{2-x})</td>
</tr>
<tr>
<td>La</td>
<td>26.4-70.4</td>
<td>1-4×10(^{17})</td>
<td>310-440</td>
<td>LaSi(_{2-x})</td>
</tr>
<tr>
<td>Ce</td>
<td>26.4-70.4</td>
<td>1-4×10(^{17})</td>
<td>295-430</td>
<td>CeSi(_2)</td>
</tr>
<tr>
<td>Pr</td>
<td>8.8-17.6</td>
<td>0.5-2×10(^{17})</td>
<td>190-260</td>
<td>PrSi(_2)</td>
</tr>
<tr>
<td>Nd</td>
<td>8.8-35.2</td>
<td>0.5-2×10(^{17})</td>
<td>165-320</td>
<td>NdSi(_2)</td>
</tr>
<tr>
<td>Sm</td>
<td>8.8-35.2</td>
<td>0.5-2×10(^{17})</td>
<td>190-390</td>
<td>SmSi(_2)</td>
</tr>
<tr>
<td>Gd</td>
<td>4.4-17.6</td>
<td>0.5-2×10(^{17})</td>
<td>100-230</td>
<td>GdSi(_2)</td>
</tr>
<tr>
<td>Tb</td>
<td>8.8-35.2</td>
<td>0.5-2×10(^{17})</td>
<td>180-340</td>
<td>TbSi(_2)</td>
</tr>
<tr>
<td>Dy</td>
<td>8.8</td>
<td>0.5-2×10(^{17})</td>
<td>190</td>
<td>DySi(_2)</td>
</tr>
<tr>
<td>Er</td>
<td>8.8-26.4</td>
<td>0.5-2×10(^{17})</td>
<td>140-260</td>
<td>ErSi(_2)</td>
</tr>
</tbody>
</table>
discuss a typical case of Dy ion implantation with a fixed current density of 8.84 µA/cm² to the doses of 0.50, 0.75, 1.0, 1.50, and 2.0 × 10¹⁷ ions/cm², respectively. Figure 2 exhibits the XRD patterns for all the implantation doses and shows the formation of the DySi₂ phase as well as its structural evolution. It is noted that the equilibrium DySi₂ phase could be formed at a relatively low temperature of 190°C, implying that the formation process upon IBS using MEVVA ion source was controllable and thus the technique would be potential for application. From the XRD patterns shown in Fig. 2(a)-(d), with increasing the implantation dose, the diffraction peaks from the DySi₂ phase became sharper or stronger, indicating that the crystalline structure of the formed DySi₂ phase was gradually improved. When the ion dose was eventually increased to 2 × 10¹⁷ ions/cm², the XRD pattern in Fig. 2(e) was basically the same as that shown in Fig. 2(d). From the above results, it seemed that there existed a certain saturated dose for ion implantation, which was sufficient for growing a well-crystallized DySi₂ phase. In our case, the nominal saturated dose was about 1.0-1.50 × 10¹⁷ ions/cm². Incidentally, such a saturation phenomenon has also been observed in other situations [14].

Figure 3 shows a RBS spectrum obtained from a Si (111) wafer implanted by Dy ions at a current density of 8.84 µA/cm² to an ion dose of 1 × 10¹⁷ ions/cm². As one can see, the signal immediately behind the Si leading edge is more or less flat and the Dy signal is relatively sharp, indicating that a very thin DySi₂ layer is formed. As there is no apparent tail at the low-energy edge of the Dy signal, the interface between the formed DySi₂ and the Si wafer might be relatively sharp. From the RBS spectrum, the thickness of the Dy+Si mixture layer was estimated to be about 35 nm by a computing program [15]. It is noted that the estimated thickness of the Dy+Si mixture was thinner than that deduced from the TRIM program by using the nominal implantation parameters. Such a significant difference could be attributed to the fact that a considerable portion of the implanted Dy atoms has been sputtered off the surface by high current Dy ions while interacting with the Si substrate. It was estimated that the retained implanted Dy ions were about 60% or a retained dose of about 6 × 10¹⁶ ions/cm². In addition, the composition profile of Dy deduced from the spectrum conformed to an approximative Gaussian distribution and an average stoichiometry of the formed DySi₂ was estimated to be Dy:Si=1:2.0 with an error of 2% at a distance of about 10 nm from the surface, confirming again the formation of the equilibrium DySi₂ phase. Besides, the irradiation enhanced diffusion and the Si atom migration could also affect the distribution of the depth profile of the Dy ions in Si.

In short, the optimal conditions for synthesizing the DySi₂ phase on Si wafers by MEVVA ion implantation were implant with a current density of 8.84 µA/cm² to a dose of approximately 1 × 10¹⁷ ions/cm².
Growth of Fractal Patterns

The MEVVA ion implantation is not only a unique technique for synthesizing metal silicides, but also a valuable means for experimental studying an interesting issue, i.e. the fractal pattern formation during the growth of the silicides upon implantation, because the implantation dose can readily be adjusted, enabling one to trace the detailed growth of the metal silicide step-by-step. SEM observations revealed some interesting features of the RE metal silicides on the Si surface after high current ion implantation.

For instance, Fig. 4 displays a set of SEM images obtained from the Si samples implanted by Er-ions with various current densities to a fixed dose of $1 \times 10^{17}$ ions/cm$^2$. One can see that the morphology of the formed ErSi$_2$ changes with the formation temperature, which corresponds to varying of the current density. At the lowest studied temperature of 140°C, corresponding to implantation with a current density of 8.8 µA/cm$^2$, an interesting network pattern consisting of ErSi$_2$ grains (the bright regions) was observed on the Si surface, as shown in Figure 4 (a), which is believed to relate to an early stage of the grain growth of the Er-disilicide. To characterize the pattern, the pattern was divided into concentric disks with various radii R. Using an image-processing computer, the pixel number N (corresponding to an area) occupied by the pattern in each disk was counted. It turned out that a linear correlation could be fitted for $\ln(N)$ versus $\ln(R)$, which collaborated the surface pattern was indeed of fractal, and the fractal dimension was thus determined. For each sample, an average fractal dimension was obtained by measuring several times on the same pattern at different locations. From Fig. 5, the fractal dimension of the above network pattern was determined to be 1.90 with a standard deviation of 0.04, which was around the percolation threshold, implying that the formed ErSi$_2$ grains become inter-connected. When the formation temperature was increased to 190°C, a plain ErSi$_2$ layer with fine ErSi$_2$ grains on the Si surface was obtained, as shown in Figure 4(b) which fractal dimension was 2.0. Further increasing the formation temperature up to 260°C, the grain size of the ErSi$_2$ layer as shown in Figure 4(c) was similar as that in Figure 4(b). It is well known that the higher the temperature the faster the crystals grow. Consequently, it was a high formation temperature yet with no adequate growing time that resulted in a dense aggregated morphology shown in Figure 4(c). To study the effect of the ion dose on the morphology of the ErSi$_2$, another Si sample was implanted by Er-ions with a current density of 17.6 µA/cm$^2$ to a dose of $2 \times 10^{17}$ ions/cm$^2$, which was twice the dose for the case shown in Fig. 4b and the observed morphology as shown in Fig. 4d. One can see that many ErSi$_2$ grains did not grow homogeneously and some bigger grains grew upright in a cylindrical shape, indicating that though the implantation was conducted with a same ion current density, an additional fluence of Er-ion

![Fig. 4. Surface morphologies of Si (111) wafers implanted by Er-ions with various conditions. (a) 8.8µA/cm$^2$, 1x10$^{17}$ions/cm$^2$, (b) 17.6µA/cm$^2$, 1x10$^{17}$ions/cm$^2$, (c) 26.4µA/cm$^2$, 1x10$^{17}$ions/cm$^2$, and (d) 17.6µA/cm$^2$,](image)

![Fig. 5. Double logarithmic plot of the fractal pattern in Figure 4(a). The characteristic fractal dimension of the network pattern was 1.90.](image)

![Fig. 6. Cross-sectional SEM image of the formed DySi$_2$ layer implanted by Dy-ions at a current density of 8.84 µA/cm$^2$ to an ion dose of 1x10$^{17}$ ions/cm$^2$.](image)
implantation would result in increasing roughness of the formed ErSi2 layers.

In order to examine the continuity of the formed RESi2 layer, cross-sectional SEM was performed for the Si sample implanted with Dy-ions with a current density of 8.8 μA/cm2 to an ion dose of 1×1017 ions/cm2. Figure 6 exhibits the cross-sectional SEM image, which clearly shows the formed DySi2 layer is continuous on the Si substrate.

**Formation Mechanism**

We now discuss the formation mechanism of the RE metal-silicide phase by high current RE ion implantation into a Si surface, which could explicit the fractal pattern growth of the formed RESi2 phase and its continuous layers. In the present study, the MEVVA ion source provided a pulsed ion beam. The time period of one pulse was 1.2 ms and the implanted RE ions triggered a series of atomic collisions among the implanted RE metal ions and the target Si atoms. According to the atomic collision theory, such a process is commonly divided into two steps, i.e. the atomic collision and followed by a relaxation, which lasts for a very short time period of 10^-10^-10^-9 s [16]. In other words, the relaxation took place after one pulse and completed within 10^-10^-10^-9 s. The time interval between the two consecutive pulses was 0.3-1.0 s, which was much longer than the relaxation time period. Having these figures in mind, we discuss the following formation mechanism for synthesizing the RE metal-silicide phase as well as the corresponding layer on Si upon high current RE metal ion implantation. For simplicity, the process was proposed to proceed in three steps for each pulsed RE metal ion implantation. In the first step, the high energy RE metal ions were dynamically launched into the Si lattice and simultaneously triggered drastic atomic collisions among the RE metal and Si atoms, resulting in a highly energetic RE+Si mixture. It is commonly recognized that during this step, the crystalline structure of the RE metal-silicide cannot be formed because a large number of atoms are in violent motion.

In the second step of relaxation, beginning at the termination of the atomic collisions, the highly energetic RE+Si mixture should somehow relax towards equilibrium, resulting in forming fine and small RE metal solicide grains in some local areas where the stoichiometry of RE metal/Si was equal/greater than 1:2. The formation of RE metal silicide phase with the simplest crystalline structure was thermodynamically favored, because it has the lowest free energy compared to other possible RE metal silicides. The third step is defined as the time period from the end of relaxation to the next implantation pulse coming in. During the third step, the already crystallized RE metal silicide grains should undergo a random walk and organize themselves to grow up. If the RE metal silicide grains could grow into a sufficiently large size before the arrival of the next implantation pulse, they are not destroyed completely by the impact of the incoming RE metal ions and can remain in the Si surface layer. When the next pulse arrives, some new RE metal silicide grains could be formed and the growth of the previously retained RE metal silicide grains could continue to proceed. The continuation of the above process results in the formation of a continuous layer, consisting of the grains of the formed RE metal silicide that eventually cover the entire Si surface, which was in agreement with a planar and continuous RE metal silicide layer shown in Fig. 6.

In RE metal ion implantation, the energetic RE metal ions were implanted into the Si lattice and this dynamic process did not require the Si substrate to be at an elevated temperature like that required in SSR. The high current RE metal ion implantation caused a simultaneously significant temperature rise of the Si substrate, which helped in forming the RE metal silicide phase. In addition, the well-known radiation enhanced diffusion (RED) could also be of help in promoting the formation of the RE metal silicide phase, e.g. reducing the formation temperature. The above three effects made it possible to synthesize the RE metal silicide phase at a considerably lower temperature upon MEVVA ion implantation than that required in SSR. Consequently, the MEVVA ion implantation requiring neither external heating during implantation nor post-annealing was an ideal technique for the formation of the RE metal silicides.

**SUMMARY**

We have shown that a series of RE metal silicides were synthesized by high current pulsed ion implantation into Si wafers using the MEVVA ion source and the structural evolution as well as the growth of fractal patterns consisting of RE metal silicide grains was induced, correlated to the substrate temperature and the dose during implantation. Furthermore, a proposal formation mechanism could possibly explain the experimental results. Technically, under appropriate conditions, continuous RE metal silicide layers on Si with fine grains can be obtained by a single-step MEVVA implantation. It is believed that MEVVA ion implantation is a promising technique and has great potential for wide application in electronic device technology.
ACKNOWLEDGMENTS

The financial aid to this study from the National Natural Science Foundation of China, the Ministry of Science and Technology of China (Grant No. G2000067207-1) and the Administration of Tsinghua University is gratefully acknowledged.

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