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Formation of SPE-$CoSi_2$ Submicron Line by Lift Off Using Selective Reaction

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Epitaxial $CoSi_2$ submicron line, as fine as 0.6 μm, is obtained by lift off using selective reaction in solid phase epitaxy. The lift-off mask consists of SiN/SiO_2 overhang structure, patterned by the conventional photolithography. At first, the silicide is formed on the mask-defined region, then shrinks and forms a submicron line. The phenomena related to the shrinkage of the silicide line and others are explained by the effects of surface energy. Calculated data as well as the experimental data show that the width of the silicide line is controlled by the initial film thickness and the initial mask space, if the formation time is enough for the reaction to be expected in thermal equilibrium.

1. Introduction

Recently, great efforts have been made to get higher speed in the Si devices. G. D. Alley pointed out[1] that the Si permeable base transistor has a possibility in good frequency performance as high as f_T=25 GH_z. However, new technologies are necessary in order to realize the above possibility. Especially, the fine patterning technique for obtaining the gate electrodes is one of the most important ones. We have shown that cobalt disilicide ($CoSi_2$) is grown on Si substrate by solid phase epitaxy[2] and the Si can also be grown on the top of the silicide to form Si/$CoSi_2$/Si double hetero structure. We have considered that the silicide is most suitable for the device fabrication, because of its lowest resistivity in the epitaxial metal silicides on Si and stability against heat treatment. However, there is such a problem as it can scarecely be etched by conventional dry etching techniques.

Table 1 shows the melting points and the boiling points of the fluoride or chloride of the W, Mo, Co and Ni, respectively[3]. In the case of W and Mo, the reacted species produced during plasma etching process are mainly fluoride or chloride of the metal or silicon. Since boiling points of the WF_6 and MoF_6 are enough low to vaporize at room temperature, the Mo or W silicide can be easily etched by dry etching techniques. On the contrary, since the melting points of the CoF_2 and $CoCl_2$ are

	m.p. (°C)	b.p. (°C)
WF_6	2	17
MoF_6	17	34
CoF_2	1200	
$CoCl_2$	730	
NiF_2	1450	
$NiCl_2$	1010	

Table 1 Melting points and boiling points of the metal fluoride or chloride.

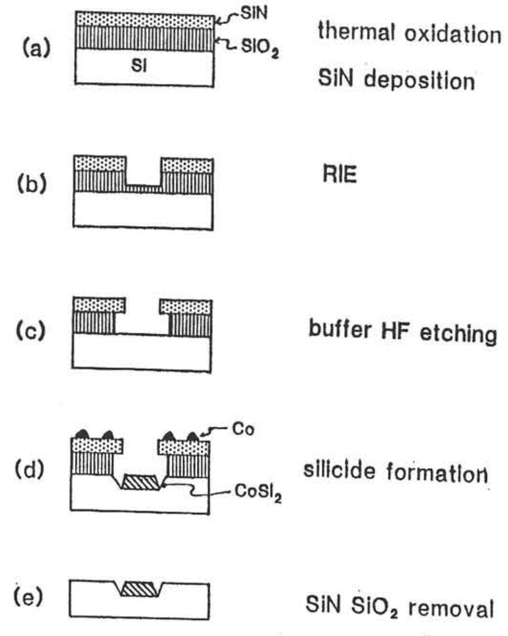

Figure 1 Experimental procedure of the LSR method.

so high that they could not easily be vapored during the etching process. For this reason, to etch the $CoSi_2$ by the dry process is more difficult than in the case the refractory metals, W or Mo, and their silicides. In this presentation, we will show a novel lift off method to obtain submicron silicide lines without any special lithographic technique. The mask for lift off consists of SiN/SiO_2 overhang structure. We call this technique as Lift off using Selective Reaction (LSR) method.

2. Experimental Procedure

Figure 1 shows the experimental procedure of the LSR method. n-type Si(111) wafers were used in the experiment. At first, the wafers were thermally oxidized by the thickness of 1 µm. Then, the silicon nitride was deposited by plasma CVD by the thickness of 400 nm as shown in (a). This sample was selectively etched by the reactive ion etching technique as shown in (b). The Al mask used for the etching of SiN and SiO_2 films was patterned by the conventional photolithography. The wafer was then dipped into buffer HF solution in order to etch only SiO_2, so as to get "over hang" mask structure as shown in (c). The width of the mask space is from about 1.5 µm to 10 µm. The sample was loaded into an UHV chamber. Then the Co was deposited at room temperature by the thickness of 29 nm, followed by annealing at 490 °C for 20 min and at 900 °C for 120 min (two step annealing method, reported at the 1983 solid state devices and material conference[4)]), as shown in (d). The region where Co deposited was defined by the overhang mask space. Finally the mask was removed by hot H_3PO_4 and buffer HF to get silicide lines on the top of Si, as shown in (e).

We had tried alternatively to make the lift off line by using only SiO_2 mask, which had no overhang structure. However, the edge of the silicide line was found to become very rough. Since the Co was partialy deposited on the side wall of the SiO_2 mask during the deposition process, the silicide formed on the side wall of the SiO_2[5)] affected the smoothness of the edge of the line. The overhang mask structure is essential to solve this problem and to get smooth line edges, because the overhang prevented the deposition of Co on the side wall of the SiO_2.

Figure 2 shows examples of the lift off lines, observed by Scanning Electron Microscopy (SEM). The silicide line of as narrow as 0.6 µm, shown by the white region in the figure[6)], has been fabricated in success by this LSR method. It should be noted that the width of the line is narrower than the gap of the mask, i.e. there happens a shrinkage of the silicide line. As shown in Fig.2(b), in case when the silicide line is relatively wider, there are hexagonal holes. However, in the case of the finer pattern, there is no holes. These phenomena can be interpreted by considering the effect of surface energy, as discussed in next section.

3. Consideration on the mechanism of surface morphology by surface energy

We reported that the uniformity of the silicide is improved by patterning silicon wafer before the silicide formation[4)]. The phenomena re-

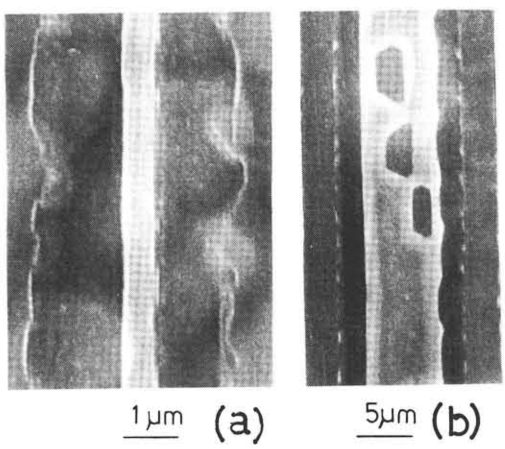

Figure 2 SEM photographs of the silicide lines. White regions correspond to the formed silicide regions.

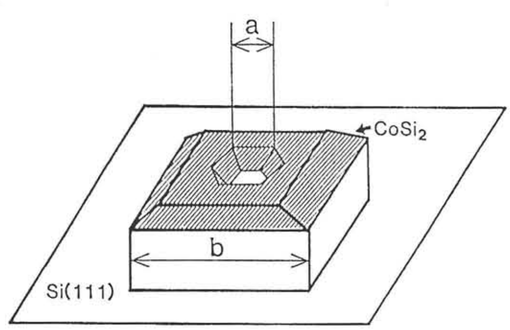

Figure 3 A model for the calculation of surface energy on squre-patterned region.

lated to patterning method can be interpreted by introducing the concept of surface energy as follows. A model shown in Fig.3 could be assumed as a reasonable one from the experimental results. The area on which silicide formed is restricted by the pattern in the form of squre, and the size of the pattern is defined by "b". In the center of the pattern, there is a hexagonal hole and the size of which is defined by "a". The surface energy of the patterned area, which is composed of the energy of the silicide (hatched area) and exposed Si region are numerically calculated as shown in Fig.4, assumed to be the surface energy as Si(111)=1.47×10^3 erg/cm^2, $CoSi_2$(111)=2.38×10^3 erg/cm^2 and $CoSi_2$(110)=2.92×10^3 erg/cm^2, respectively. When "a", the length of the pattern, is less than 3 µm, the energy have monotonously increased as a function of "a". It means that even if holes were at the first step in the process, the film would tend to be uniform. This is because the system tends to reduce its total surface energy. On the otherhand, when "a" is more than 4 µm, the energy decreases with increasing of the hole size, "a". It means that the film would not become uniform if it had once hole at the first step in the process. The critical value for "a", in less than which the film could become uniform is calculated as 3.5 µm.

Figure 5 shows the critical lengths of pattern side as a function of the initial silicide thickness. The calculated values denoted by a solid line, shows a linear relation. It can be said that the experimental data denoted by the broken line almost agree with the theoretical values, even though there is some quantitative discrepancy. At least, it is noted that both experimental and theoretical values show linear relations with the thickness of silicide films. This indicates that the effect of patterning is explained in principle by the above surface energy model. The quantitative discrepancy between the theoretical and experimental values is considered to be due to first order assumption on the values of energies of $CoSi_2$ and Si in theoretical calculation. The difference of film uniformity on the width of silicide lines, as shown in Fig.2, also can be explained by using concept of the surface energy, that is, by using the almost same argument related to Fig.4. Anyway, such tendency as narrow silicide line has no hole, is very useful to fabricate devices having good performances at high frequency.

4. Application of the theory to LSR method

We shall also try to understand the phenomena of the shrinkage in the silicide lines by using the surface energy. The surface energy of the silicide line is calculated as shown in Fig.6. The inset shows the model used for the calculation. The model shows the crossectional view of the sample. At first, the Co was deposited on the defined area, of which width is L. During annealing process, at first the silicide is formed at the defined area, indicated by "L". Next, the

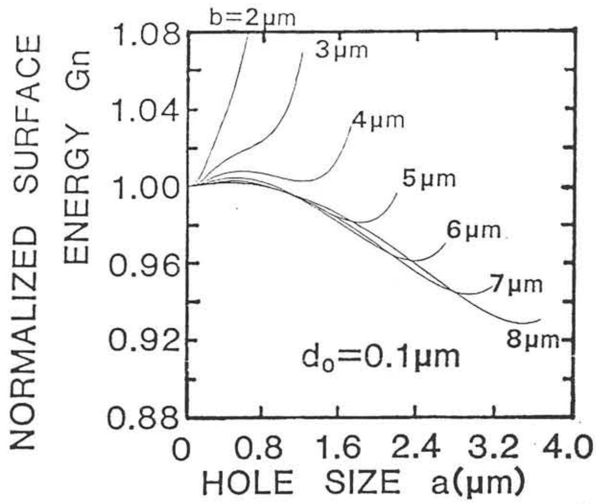

Figure 4 Calculated surface energy of the squre-patterned region as a function of the hole size "a". The energy is normalized by the energy in the case when there is no hole (a=0).

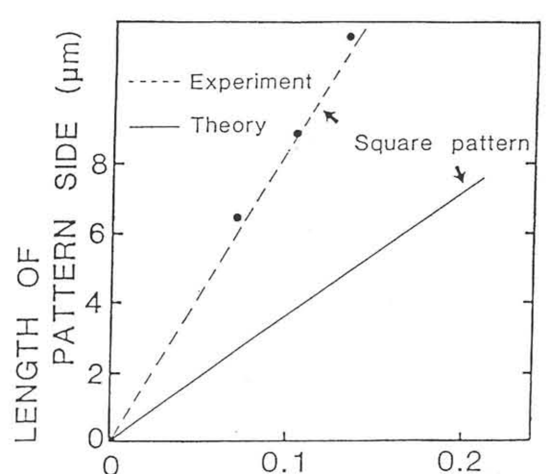

Figure 5 Theoretical and experimental results of the critical lengths of pattern side as a function of the initial silicide thickness.

silicide is assumed to be shrinked by the width of "b" (hatched region). The surface energy, normalized by the surface energy of 10 μm width Si(111) surface, is indicated as a function of "b" in this figure. At first, the surface energies decrease when the width of the silicide lines become smaller. It indicates that the silicide line would naturally be shrinked so as to decrease its surface energy.

It is interesting that the energies in the above calculation have the minimum values at certain values of "b". We can say that these values of "b" give the thermal equilibrium widths of the silicide lines. Figure 7 shows the line widths corresponding to the thermal equilibrium conditions as a function of the initial line width. The experimental data are taken by using the sample, which has been prepared at almost thermal equilibrium condition (900 °C, 4 h annealing). Good agreement between theoretical and experimental values is obtained as shown in the figure. It can be said that the phenomena of the shrinkage of silicide lines are also determined so as to keep the minimum surface energy in the system. We would like to note that the reproducibility of the final line width is fairly good, if the initial thickness and width of the silicide line are accurately defined.

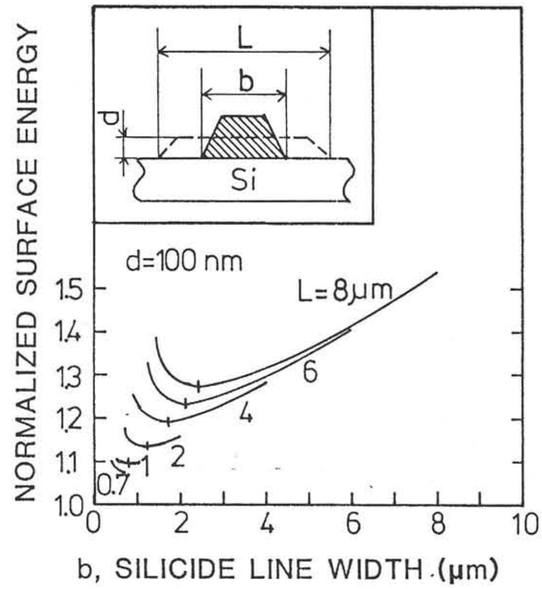

Figure 6 Surface energy as a function of the silicide line width. The inset shows a model, which identifies with the cross section of the sample, for the calculation. The energy is normalized by surface energy of 10 μm width Si(111) surface.

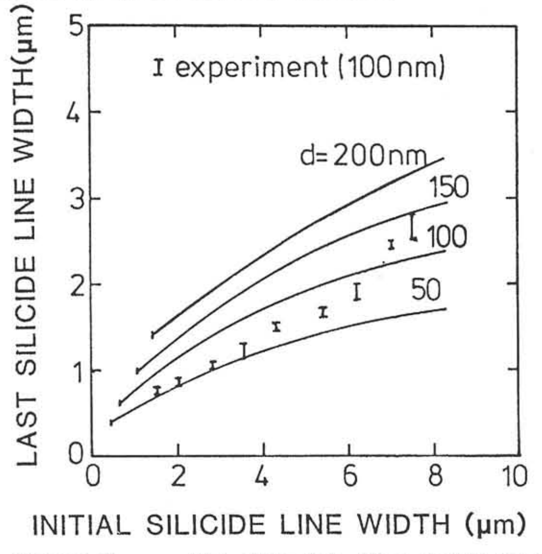

Figure 7 The silicide line width coresponding to the thermal equilibrium condition as a function of the initial line width.

5 Conclusions

1) We have fabricated silicide lines by LSR method in success as fine as 0.6 μm without any high level lithographic technique.

2) We have shown experimentally and theoretically that the phenomena of the surface morphology of the silicide film can be explained by the concept of surface energy.

3) The width of the silicide line can be controlled accurately by only adjusting the initial silicide thickness and width, because the thermal equlibrium condituion of the silicide in the process can be used.

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