

Study on Formation of Solid-Phase-Epitaxial CoSi₂ Films and Patterning Effects

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Formation of CoSi₂ by solid phase epitaxy are investigated. When the film is formed by conventional SPE method, the film is not usually uniform and surface of the sample is consisted of both Si area and formed CoSi₂ area. Two step annealing method proposed is effective to improve the uniformity of the film, e.g. the Si area is drastically decreased. Patterning of Si wafer before silicide growth is also effective to improve the uniformity. The growth kinetics of the silicide is also discussed.

1. Introduction

It has been reported that CoSi₂ grow epitaxially on silicon substrates by solid phase epitaxy or molecular beam epitaxy, and Si films grow on the crystalline CoSi₂ films to form a semiconductor/metal/semiconductor double heterostructure^{1),2)}. By this structure, it is possible to fabricate novel devices such as the metal base transistor, the permeable base transistor and the buried gate static induction transistor. In addition to these applications, the double heterostructure has a possibility to be used for 3-dimensional integrated circuit.

From the practical view point, the SPE might be better than MBE, because SPE has a possibility of low temperature process and good productivity. However, when a CoSi₂ film was grown by a conventional SPE method, the uniformity of the film is not so good, but the film often breaks and the substrate Si is exposed as shown in Fig.1. In this figure, the steps of the sample surface are just the silicide thickness. We have investigated this film by Rutherford backscattering spectroscopy and micro-probe auger electron spectroscopy^{3),4)}, and found that dark regions correspond to exposed Si regions, and the bright region corresponds to a formed silicide region.

In this paper, two novel method will be shown to obtain more uniform films than those by the conventional SPE method. In addition to this,

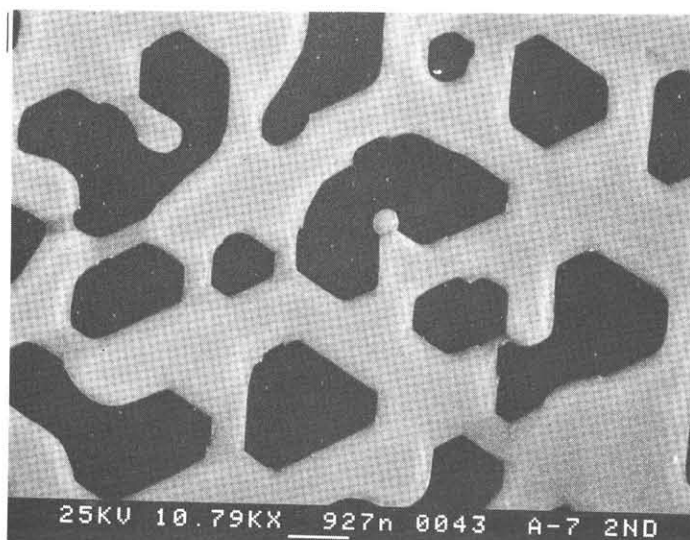


Figure 1. A SEM photograph of the sample formed by the conventional SPE method. The steps of the surface is about 100 nm, which is just the silicide thickness. The dark regions are substrate Si areas, and the bright region is formed silicide region.

mechanisms of those phenomena will be discussed.

2. Two step annealing method

Figure 2 shows experimental procedures of the direct annealing method (conventional method) and the two step annealing method. n-type Si(111) wafers were chemically cleaned by solution of H₂O₂:HCl:H₂=1:4:1⁵⁾, and loaded in a vacuum chamber equipped with ion pumps, E-gun evaporator and two 500 W halogen lamps. At first, the samples were heated at a temperature of 750 °C to clean thermally the surface by the halogen lamps. The Co films about 30 nm thick were deposited by E-

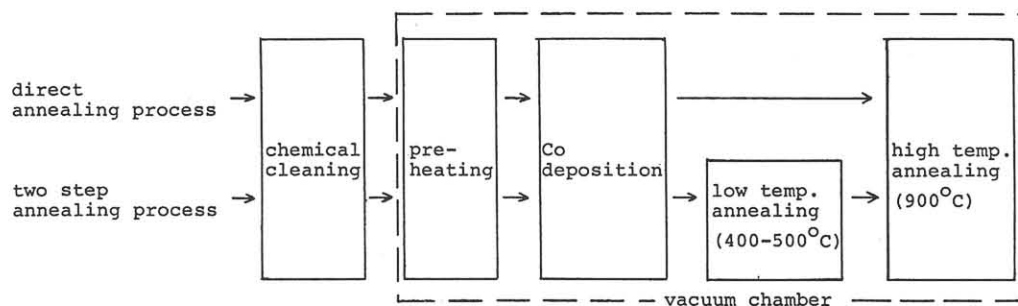


Figure 2. Experimental procedure of direct annealing process (conventional method) and two step annealing process.

gun. In the case of the direct annealing method, the samples were directly annealed at 900 °C for 30 min to form epitaxial CoSi_2 layer. In the case of two step annealing method, the Co deposited samples were annealed at low temperatures ranging from 400 to 500 °C to form CoSi at first, and followed by annealing at 900 °C for 30 min to form epitaxial CoSi_2 films.

The film uniformity is evaluated by the exposed Si area normalized by the whole area, which is designated by R_{Si} , from the SEM photographs of samples as shown in Fig.1. The crystallinity is evaluated by the aligned yields normalized by random yields in backscattering spectrum, which is designated by χ_{min} . Figure 3 shows the R_{Si} and χ_{min} values after the second annealing process as a function of the first annealing temperature. As shown in this figure, R_{Si} decreases from about 36% for the direct annealing process (conventional method) to 5-10% for the two step annealing process, with the first annealing temperatures from 450 to 490 °C. χ_{min} also decreases in these temperature range. As a result, it is clear that the crystallinity as well as the uniformity can be improved by the two step annealing process.

3. Growth Kinetics

We observed initial stages of the silicide formation in order to understand the reason of the silicide breaking and Si exposing in a part of sample surface. It has been found by consulting the backscattering spectrum in detail that, when the deposited film was annealed at 900 °C for 20 sec, the stoichiometry of the formed silicide is CoSi_2 but the film haven't been epitaxially grown on the substrate. In addition, many grains at size of sub micron were observed by SEM. Then, the formed silicide was poly-state CoSi_2 .

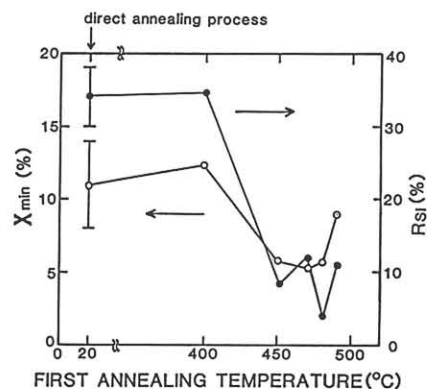


Figure 3. R_{Si} and χ_{min} values after the second annealing process as a function of the first annealing temperature.

Figure 4 shows the SEM photograph and the backscattering spectrum of the sample annealed at 900 °C for 60 sec. Some grains as well as some islands can be seen in this photograph. An aligned yield of the channeling experiment for this sample is about 2/3 of that of random spectrum, and the top part of the aligned spectrum is almost flat. It means that the film grew epitaxially in part and the islands in Fig.4 are epitaxial grown parts of the film.

In the case of two step annealing, the initial stage of the silicide growth is quite different from that in the case of direct annealing process. Figure 5 shows the backscattering spectra of the sample annealed at initial low temperature annealing. From this spectra, the formed silicide is calculated to be almost CoSi , but near the interface of the film between silicide and substrate Si, the silicide CoSi_2 start to grow epitaxially.

We give to this phenomena an interpretation as follows; It is reported that CoSi start to grow after Co_2Si formation.⁶⁾ Since Co atom is dominant diffusion species in Co_2Si , the contamination is considered to move toward the surface like inert

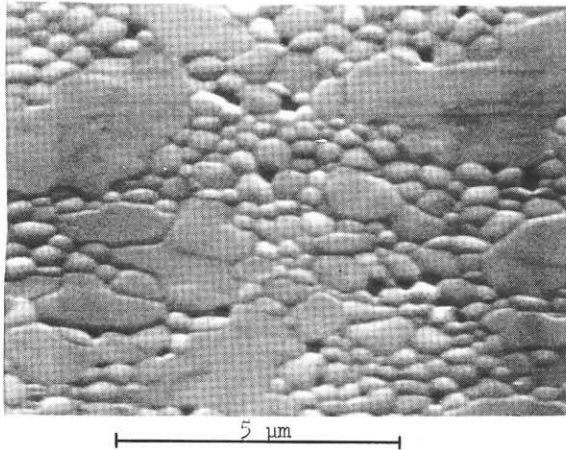


Figure 4 A SEM photograph and the backscattering spectrum of the sample annealed at 900 °C for 60 sec.

atoms in the marker experiment⁷⁾. As a result, the interface between CoSi and Si substrate become clean to realize good growth conditions for the solid phase epitaxy. On the contrary, the dominant diffusion species is silicon atom in CoSi₂, so the contamination is considered to move toward the interface. As a result in the direct annealing process, the contamination at the boundary between poly-CoSi₂ and Si substrate will disturb the solid phase epitaxy of CoSi₂ to let the silicide coalesce as shown in Fig.4, so that the uniformity is not good.

4. Patterning effect of Si wafer for silicide formation.

In the second method, the surfaces of the wafers were patterned before silicide formation. Using the conventional photolithograph technique and plasma etching process, the wafers were selectively etched at depth of 1.4 μm to form stripe or checker patterns as schematically shown in Fig.6. Then the silicide was formed by the two step annealing process on the wafers.

Figure 7(a) shows the optical micrograph using Nomarski interference contrast for various pattern width. The region designated by an inset in Fig.7(a) was observed by SEM as shown in Fig.7(b). By comparing an optical micrograph and SEM photograph, the deep holes which can be seen in Fig.7(a) identify with exposed Si areas. It can be seen more clearly from these figure that the narrower the pattern is, the less the exposed Si areas become. It is to be noted that the coverage of the silicide is quite poor in the

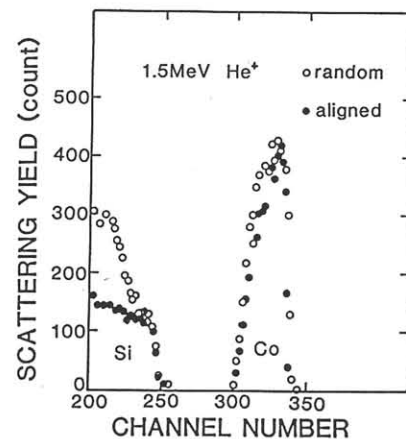
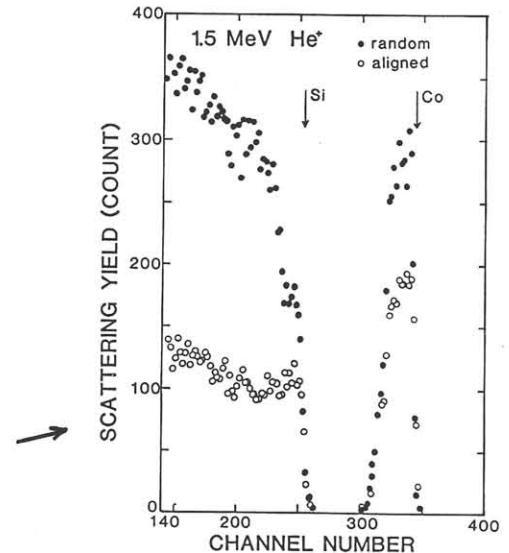


Figure 5 A backscattering spectrum of the sample annealed at 490 °C for 20 min.

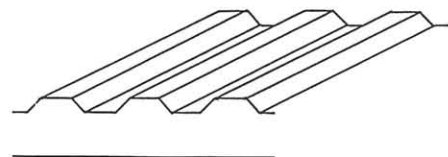


Figure 6 A schematic of a patterned Si wafer.

slope regions just outside of the patterns. At just edge parts of the pattern, the silicide is thicker than other part.

Figure 8 shows the R_{Si} as a function of the stripe and checker width. We can say from this figure that the exposed Si area can scarcely found for the cases when patterns become smaller than 7 μm and that the checker pattern is more effective than the stripe patterns when the size is larger than 10 μm. Figure 9 shows the example of

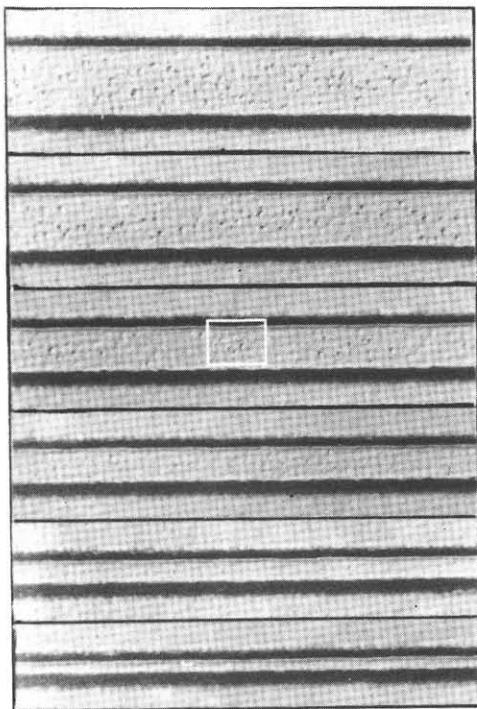


Figure 7(a)

the checker pattern. At the edge of the pattern the silicide swell up like stripe pattern, but an almost uniform film free from the exposed Si region about 16 μm was obtained.

5. Conclusions

- 1) The uniformity and crystallinity of solid-phase epitaxial CoSi_2 films was improved by the two step annealing process.
- 2) Exposing of Si area during silicide formation is considered due to coalescence of poly CoSi_2 grain and interface contamination. The contamination
- 3) Patterning Si wafer is effective to improve the uniformity of the film.

Acknowledgement

Authors are gratefully thankful to Prof. Iga of TIT and Mr. Idegumori of Akashi Application Center for observation by SEM. A part of this work was supported by the grant-in-aid for special project research (No. 57117001) from the Ministry of Education, Science and Culture of Japan.

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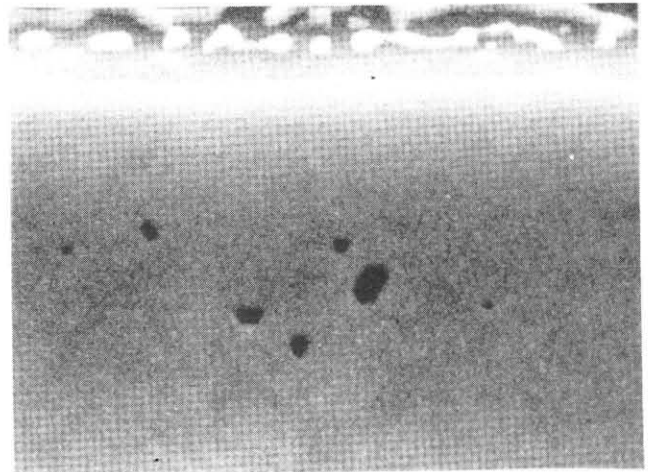


Figure 7(b)

Figure 7 Optical micrographs and SEM micrographs of the silicide on the stripe patterns. A inset in (a) is observed by SEM as shown (b).

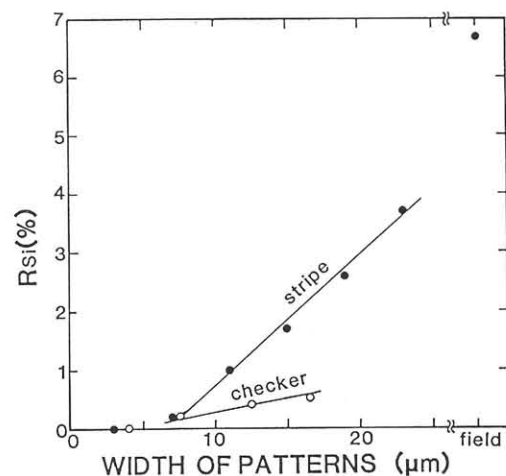


Figure 8 R_{Si} value as a function of pattern width.

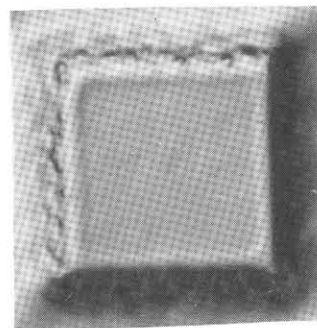


Figure 9
An optical micrograph of the silicide on a checker pattern. The size of this pattern is about 16 μm .

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