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AUTHOR(S) Fereydoon Namavar
N. M. Kalkhoran
J. M. Manke
L. Luo
J. T. McGinn

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DEPENDENCE OF BURIED $CoSi_2$ RESISTIVITY ON ION IMPLANTATION AND ANNEALING CONDITIONS[1]

Fereydoon Namavar*, N.M. Kalkhoran*, J.M. Manke*, L. Luo**, and J.T. McGinn***
* Spire Corporation, Bedford, MA 01730-2396
** Los Alamos National Laboratory, Los Alamos, NM
*** David Sarnoff Research Center, Princeton, NJ

ABSTRACT

We have investigated the dependence of electrical and material properties of buried $CoSi_2$ layers on Co^+ implantation and annealing conditions. The results indicated that the electrical resistivity and crystalline quality of the implanted buried $CoSi_2$ layers depend strongly on the implantation temperature. $CoSi_2$ layers with the lowest resistivity and best crystalline quality (χ_{min} as low as 3.6%) were obtained from samples implanted at 300°C-400°C. Implantation at higher temperatures (e.g., 580°C) produced cobalt disilicide layers with significantly higher electrical resistivity and a χ_{min} of about 10.7%.

INTRODUCTION

Series-connected vertical multijunction cells [1-7] comprised of $CoSi_2$/n-Si/p-Si/$CoSi_2$ heterostructures, with highly conductive buried $CoSi_2$ layers as interconnects, may be fabricated using high energy Co^+ implantation and annealing, and a doped-Si epitaxial growth process. These structures may be used efficiently as photovoltaic energy converters for high power density 1.06 μm output of a Nd:Yag laser. Two important considerations for fabricating such structures are: a) the crystalline quality of the $CoSi_2$ layer and its electrical conductivity, and b) the growth of high quality doped epitaxial silicon for high efficiency pn junction cells. Therefore, evaluation of the resistivity of $CoSi_2$ layers produced by various ion implantation and annealing processes, and the quality of the contact these layers form with the adjacent p-type and n-type silicon, is necessary.

In recent years, cobalt disilicide by ion implantation has been studied by a number of authors [8-10]. In the present work, we have primarily studied the effect of implantation and annealing temperatures on the formation of buried $CoSi_2$ layers, because from a device aspect, a low-temperature process is desirable. The material quality and the electrical properties of the implanted layers have been evaluated using different characterization techniques. Our experimental results indicate that high quality $CoSi_2$ layers with low electrical resistivity, suitable for usage as buried conductors for series connected vertical multijunction cells, may be fabricated using an ion implantation and annealing process.

EXPERIMENTAL PROCEDURE

Cobalt was implanted into four-inch Si(100) substrates with doses ranging from 1 x 10^{15} to 5 x 10^{17} Co^+/cm^2 at energies ranging from 160 to 190 keV and beam currents from 200 to 700 mA. Implantation temperatures ranged from 200°C to 580°C. The implantations were performed using a Varian DF4 medium current implanter, a Varian 200-1000 mass analyzed

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implanter and an Eaton NV 10-160 beam generator joined to a specially-designed endstation. Pieces of each wafer were then annealed for one to eight hours at temperatures ranging from 700 to 1000°C in an N_2 ambient.

As-implanted and annealed samples were analyzed by Rutherford backscattering spectroscopy (RBS/channeling), X-ray diffractometry (XRD), extended X-ray absorption fine structure (EXAFS) analysis [11], and cross-sectional transmission electron microscopy (XTEM). The electrical resistivity of as-implanted and annealed samples was measured in vacuum at temperatures ranging from 150°K to 295°K using a variable temperature conductivity measurement system (VTCMS), which includes a collinear four-point probe mounted on a free-standing cold plate in a vacuum chamber. A direct current was passed through the sample, and the resulting potential difference was measured as a function of temperature using an electrometer. All meters, including thermocouple and vacuum gauge meters, were computer-controlled.

EXPERIMENTAL RESULTS

We have extensively investigated Co^+ implantation into Si at temperatures of 200°C-580°C. Here, we discuss only results of implantations carried out at 580°C and at 300°C-400°C.

Implantation at 580°C

Figure 1 compares the measured electrical resistivity as a function of temperature, in the 150°K-295°K range, for as-implanted and annealed pieces of a Co^+-implanted Si wafer. The high resistivity of the as-implanted sample is related to the damage (Figure 2) and the lack of stoichiometry for the buried $CoSi_2$ layer. The RBS results (Figure 3) indicated that the Co:Si ratio for the as-implanted sample is much less than 1:2. On the other hand, the X-ray, electron diffraction and EXAFS results indicated the existence of the $CoSi_2$ phase. Therefore, we believe that the buried layer consists of Si as well as $CoSi_2$ microcrystals. Upon annealing, cobalt moves from greater depths, as well as from the near surface region, to the area of peak cobalt concentration to form a continuous uniform $CoSi_2$ layer. When a continuous buried layer forms, the resistivity of the sample is reduced by more than an order of magnitude

XTEM of a sample annealed for two hours at 700°C (Figure 4a) indicated a large number of threading dislocations in the silicon top layer. The top interface of the $CoSi_2$ exhibited 100Å of roughness but was generally well-defined. Within the substrate, a defect region containing a tangle of dislocations extended 2200Å below the $CoSi_2$, and end-of-range damage in the form of dislocation loops is observed at a depth of 3900Å below the $CoSi_2$. The lower interface of the $CoSi_2$ is well defined, but numerous faceted peaks extended up from the silicon substrate. Variations observed in the $CoSi_2$ layer thickness resulted largely from the irregular lower interface.

Figure 3 compares the RBS depth profile of cobalt for the as-implanted sample and the samples annealed for different periods of time at 700°C and 900°C. As shown, only a slight Co diffusion occurs after annealing for two hours at 700°C. However, this annealing schedule resulted in a significant decrease (by about one order of magnitude) in the electrical resistivity as compared to the as-implanted sample. The sample annealed for four hours at 700°C showed even lower resistivity. As shown in Figure 3, a thin $CoSi_2$ layer forms after annealing for four hours, and the cobalt peak distribution at each interface becomes very distinct.

XTEM of the sample annealed at 900°C (Figure 4b) indicated a layered structure similar to that of the sample annealed at 700°C. The RBS results showed a stoichiometric $CoSi_2$ buried layer. The resistivity and channeling results (Figure 5) indicated a large decrease in the

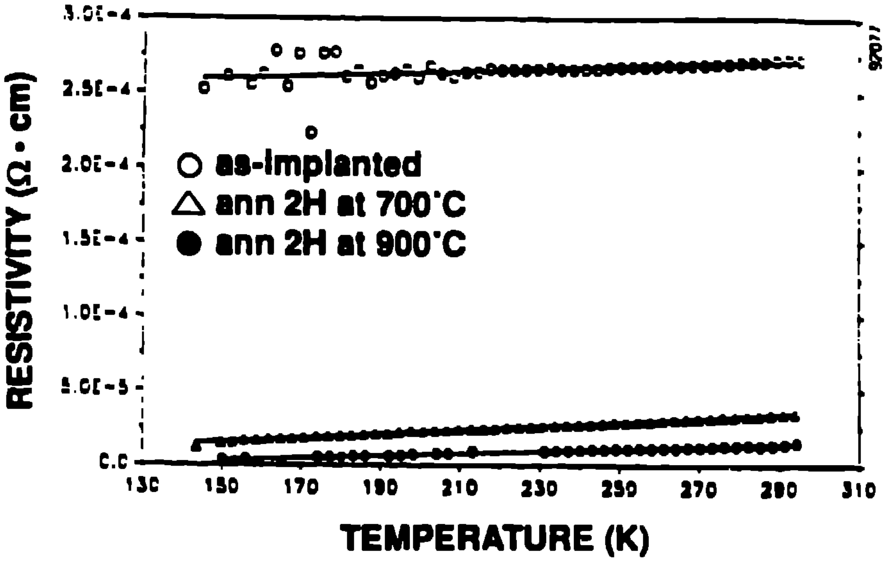


Figure 1 *Comparison of measured electrical resistivity as a function of temperature for as-implanted and annealed pieces of a Si wafer implanted with Co⁺ at 580°C*

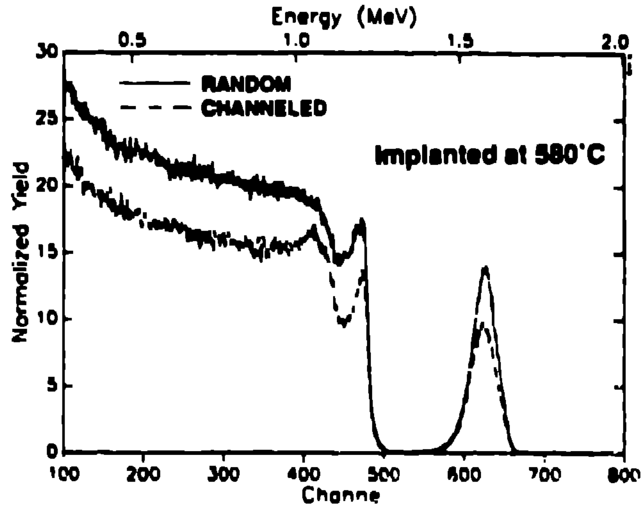


Figure 2 *Random and channeled spectra of sample implanted at 580°C, indicating a χ_{min} of 65.5%*

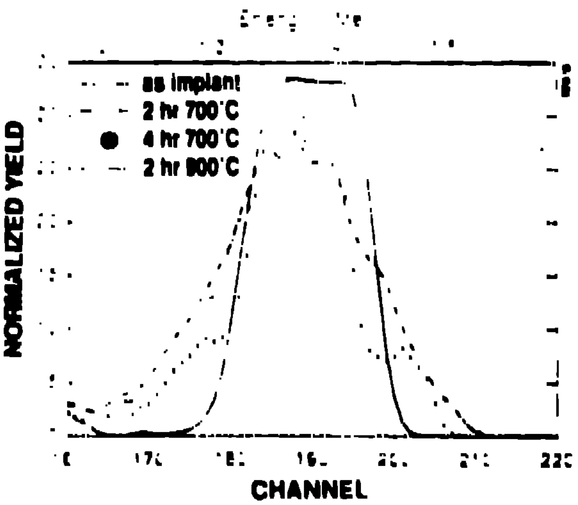
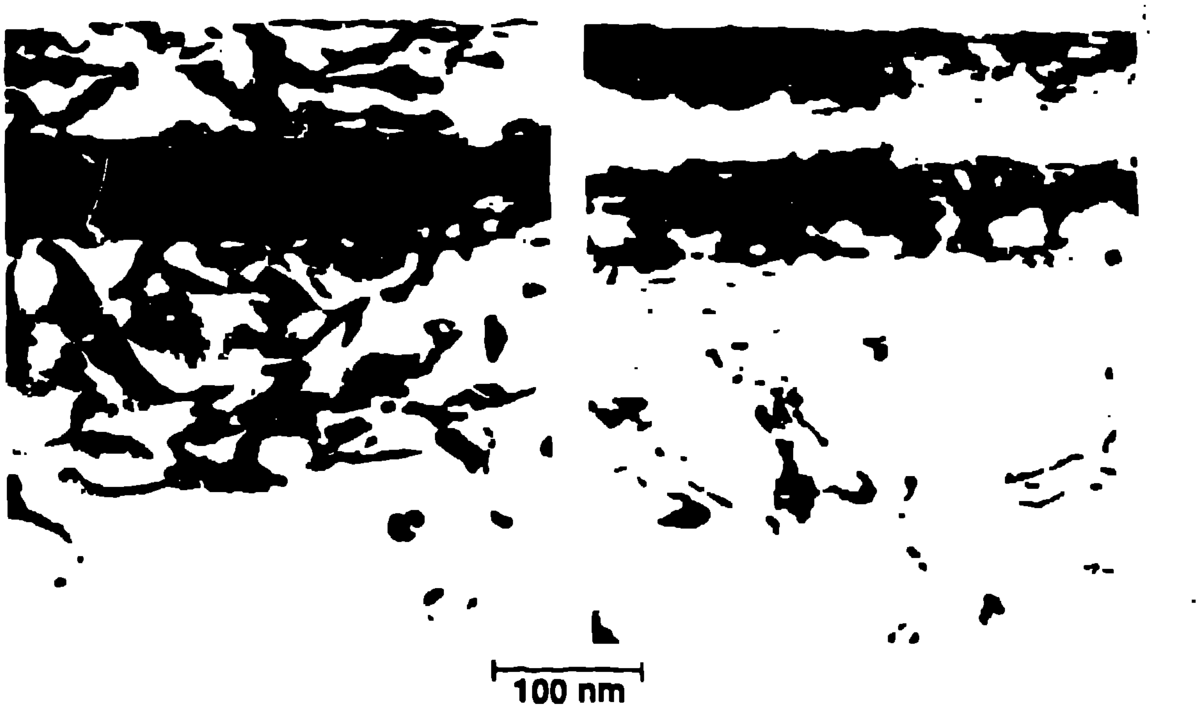


Figure 3 *RBS of cobalt in the as-implanted and annealed pieces of the Si wafer implanted at 580°C*



(a) Annealed at 700 °C (b) Annealed at 900 °C

Figure 4 *XTEM of a sample implanted at 580°C and annealed for two hours at a) 700°C, b) 900°C. Note the high dislocation density in the Si above and below the $CoSi_2$ layer.*

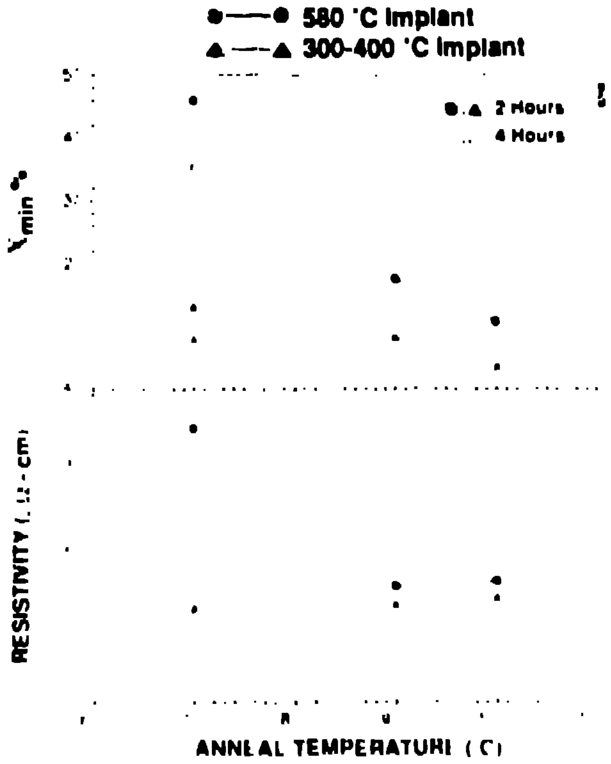


Figure 5 *Measured channeling and resistivity as a function of annealing temperature for Si samples implanted at 580°C or at 300-400°C and annealed for two or four hours.*

resistivity after annealing for two hours at 900°C. A sample annealed at 1000°C for one hour had a resistivity very similar to that of the 900°C-annealed sample. This suggests that annealing above 900°C does not change the electrical properties of the silicide layer, and also that the integrity of the sample remains intact for temperatures up to 1000°C.

Low Temperature Implantation (300-400°C)

We implanted several four-inch Si wafers with a dose of 2×10^{17} Co^+/cm^2 at 160 keV. The implantation was carried out at a temperature of about 300°C and a finishing temperature of about 400°C - from a device fabrication aspect, it is important to develop a process which will result in high quality material while requiring a low temperature process. The RBS profiles of cobalt in the as-implanted and annealed samples are shown in Figure 6. The resistivity of the as-implanted sample described above is about 27 ohm-cm, almost 10 times lower than that of the sample implanted at 580°C. This lower resistivity can be better understood by examining the RBS and channeling spectra of the samples implanted at the lower temperature (Figure 7). The Co:Si ratio of the as-implanted sample is very close to that of bulk $CoSi_2$, and the $CoSi_2$/Si interfaces appear to be very sharp and well-defined. χ_{min} for Co is about 13.4%. After annealing for two hours at 700°C and 900°C, very little redistribution of cobalt has occurred. The resistivity, however, is reduced by a factor of 2.5 when the sample is annealed for two hours at 700°C as compared to the as-implanted sample. It is important to note that no difference in the resistivity of the samples as a function of annealing time or temperature was observed, within experimental error (Figure 8).

The above results indicate that annealing at 700°C for two hours is sufficient to form a Si/$CoSi_2$/Si heteroepitaxial structure with a highly conductive $CoSi_2$ layer. It also appears that implantation at lower temperatures results in a better quality buried silicide layer than implantation at high temperatures because of the increased probability of a fine dispersion of precipitates. During the post-implantation anneal, these small precipitates facilitate the formation of a continuous, uniform buried silicide layer. XTEM of a typical sample implanted at low temperatures (about 300-400°C) (Figure 9) showed the formation of high quality heteroepitaxial Si/$CoSi_2$/Si heterostructure. No defects were observed at either the lower or upper $CoSi_2$/Si interface.

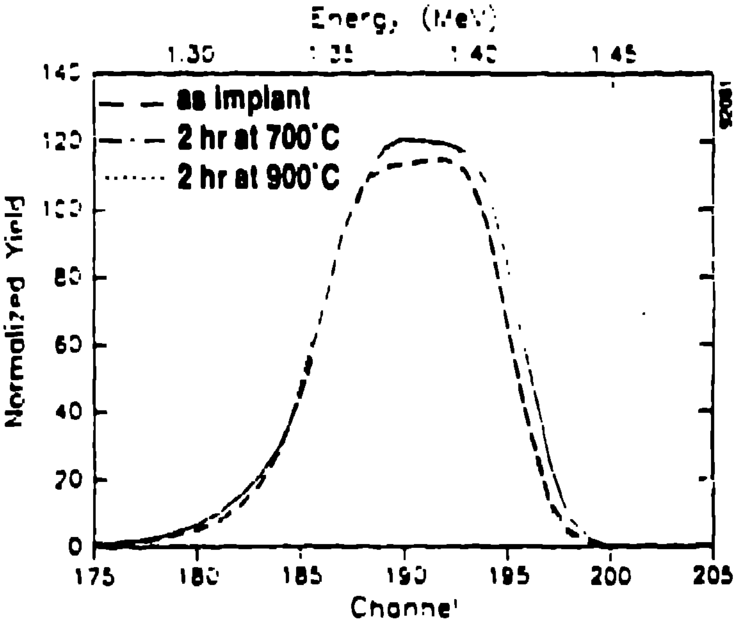


Figure 6 *RBS depth profile of cobalt in the as-implanted and annealed pieces of the Si wafer implanted at 300-400°C*

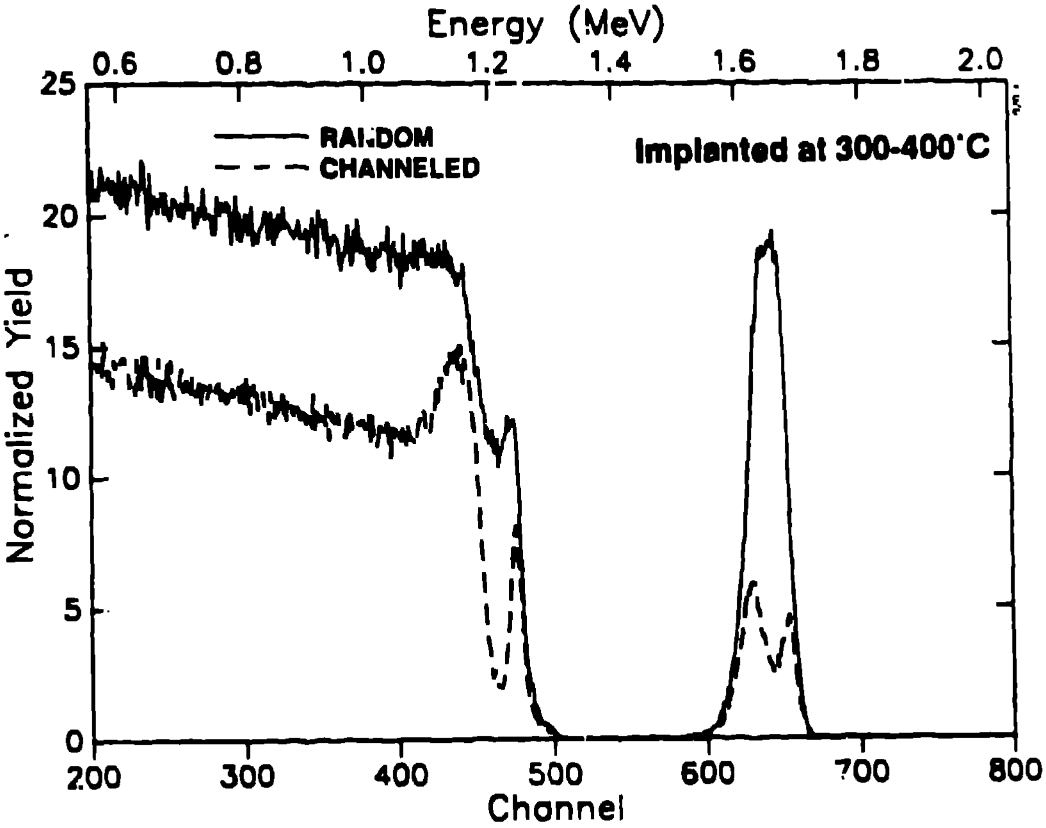


Figure 7 *Random and channeling spectra of a sample implanted at 300-400°C. Note that the χ_{min} of 13.4% for this sample is much lower (by a factor of 5) than that for the sample implanted at 580°C (Figure 2)*

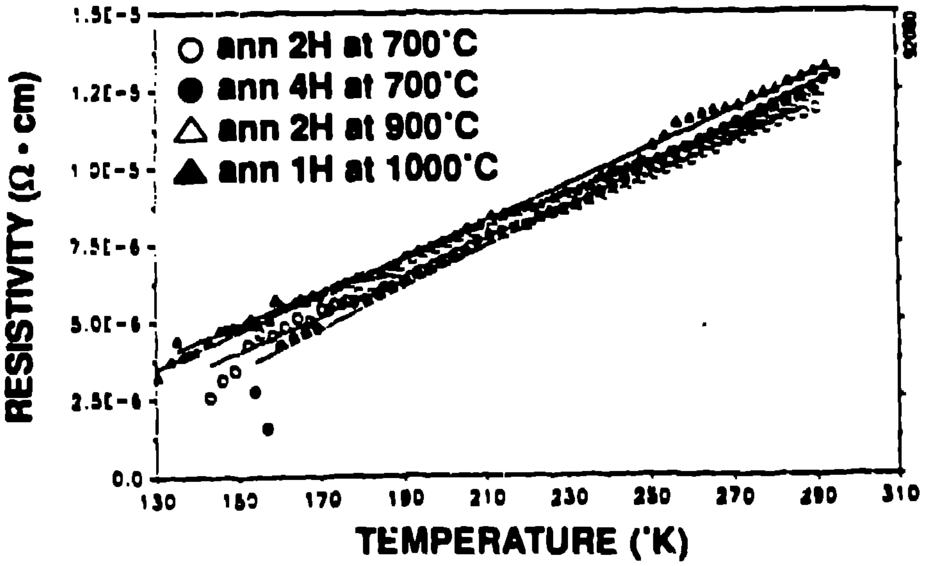


Figure 8 *Comparison of measured electrical resistivity as a function of temperature for as-implanted and annealed pieces of the Si wafer implanted with Co^+ at 300-400°C*

DISCUSSION AND CONCLUSIONS

We have demonstrated the formation of a continuous, uniform $CoSi_2$ layer produced by ion implantation at energies of 160-180 keV, followed by annealing. Our results clearly indicate that implantation temperature is the most important parameter influencing the final quality of the $CoSi_2$ layer. Comparisons of the resistivities of samples implanted at high (580°C) and low (from 300°C start to 400°C finish on the same sample) temperatures and annealed under various conditions have shown that implantation at temperatures of 300-400°C results in the formation of better quality $CoSi_2$ than implantation at 580°C. Cobalt implantation at 300°C-400°C followed by annealing at 700°C was determined to be sufficient for the formation of a continuous, uniform silicide layer with abrupt interfaces to the silicon layer and a resistivity of about 12 ohm-centimeters at room temperature.

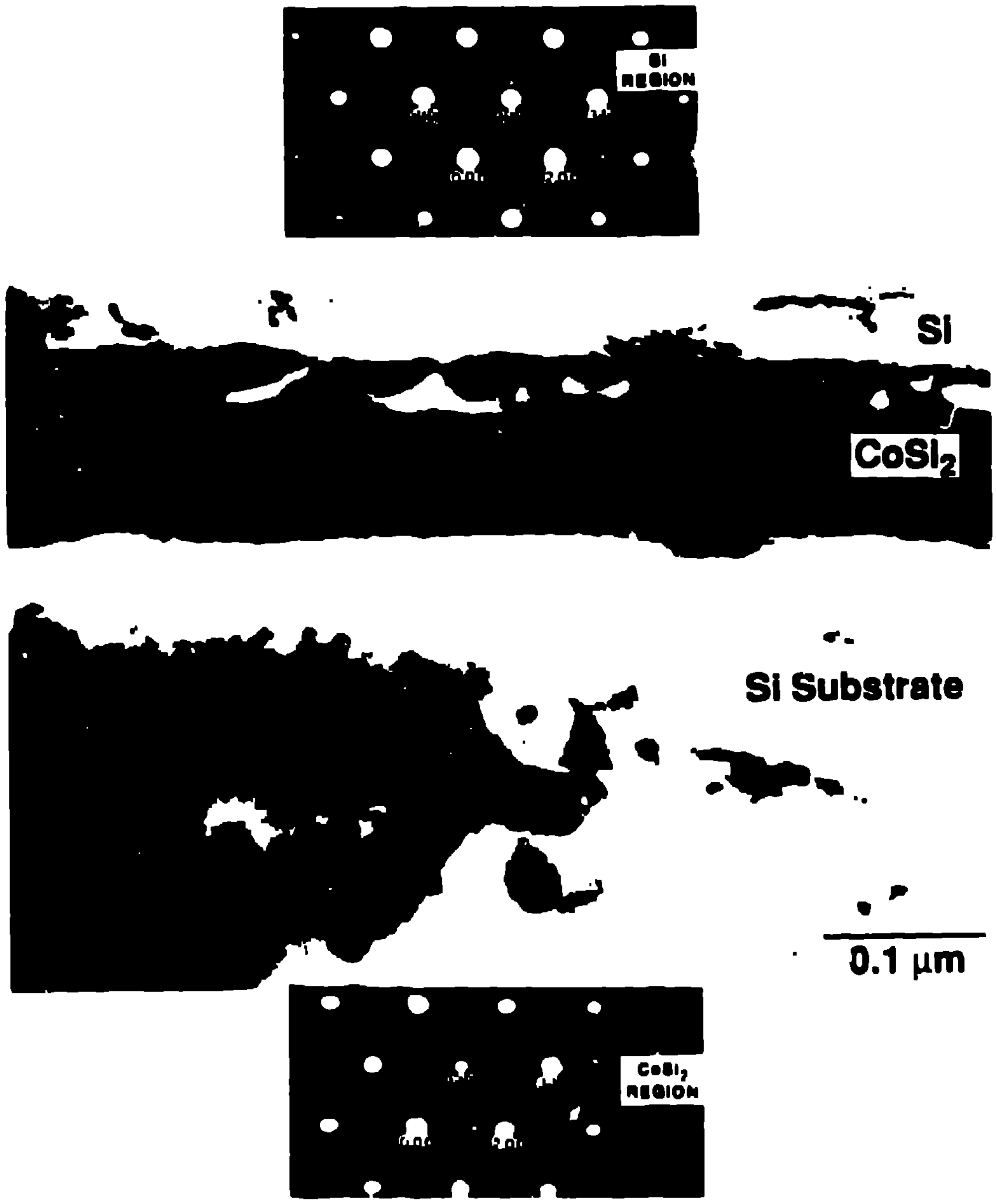


Figure 9 *XTEM and electron diffraction results from a sample implanted at low temperatures indicating the formation of a high quality Si/CoSi₂/Si heteroepitaxial structure*

$CoSi_2$ layer formation in silicon appears to be very similar to the formation of SiO_2 layers in silicon by implantation of oxygen. Work with the formation of buried SiO_2 layers by ion implantation of oxygen [12-13] has indicated that two processes are in competition during oxygen implantation. These are the nucleation and the growth of precipitates. Due to increased damage at low temperatures, the probability of nucleation is higher than the probability of growth. The increase in damage sites enhances trapping of ions and thus nucleation. On the other hand, at higher temperatures implanted ions diffuse rapidly and assist in the growth of already formed precipitates. The implantation of oxygen at low temperatures results in the fine dispersion of precipitates. This simplifies the formation of a uniform and continuous buried layer during subsequent high temperature annealing.

For cobalt silicide formation by implantation of Co^+, high temperature implantation appears to result in the formation of large precipitates. As indicated by RBS/channeling and resistivity data for samples implanted at 580°C, a higher annealing temperature and longer anneal time is required to form a continuous buried layer. Beginning implantation at a lower temperature (300°C) encourages nucleation of a fine dispersion of $CoSi_2$ precipitates, and completing implantation at a higher temperature (400°C) reduces the probability of defect formation in the silicon top layer.

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