Defect induced formation of CoSi$_2$ nanowires by focused ion beam synthesis

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Cobalt implantation with a focused ion beam (FIB) was applied to study ion beam synthesis of cobalt disilicide nanowires in silicon. Two mechanisms of CoSi$_2$ nanowire formation were investigated: (a) conventional synthesis by Co$^{++}$ FIB implantation at elevated temperatures into silicon along in-plane (110) Si crystal direction and subsequent annealing and (b) self-aligned CoSi$_2$ nanowire growth in cobalt supersaturated silicon on FIB-induced defects at room temperature during subsequent annealing. The obtained CoSi$_2$ nanowires are 20–100 nm in diameter and several micrometers long. © 2006 American Institute of Physics. [DOI: 10.1063/1.2400068]

One-dimensional crystalline nanostructures such as semiconducting (Si, Ge, GaN, and InP) and metallic (Au and Ag) nanowires (NWs) have been intensively studied in the past decade. It is advantageous for device application if it is possible to produce the desired NWs directly on or under the surface of suitable substrates, e.g., silicon wafers. By means of optical or electron beam lithography submicron silicidic structures have been made. These materials are used as low-resistive contacts, gates, and interconnecting lines in very-large-scale integrated circuits. Many efforts have been made to fabricate silicidic nanostructures employing the bottom-up approach without elaborate microlithography. For instance, the spontaneous and self-aligned growth of 3–10 nm thick CoSi$_2$ NWs from Co nanoparticles deposited onto the Si surface was described. CoSi$_2$ NWs have been reported utilizing different techniques, such as implantation based ion beam synthesis (IBS) and mesotaxy leading to the formation of wires by growth and coalescence of silicide precipitates during high-temperature annealing. Focused ion beam (FIB) implantation of Co$^+$ ions and subsequent conventional as well as flash lamp annealing were reported to synthesize nanostructures and NWs with feature dimensions of about 200 nm. In this letter the formation of CoSi$_2$ NWs in silicon using FIB IBS and the influence of the defect generation during FIB implantation on the NW growth will be reported.

(100)- and (111)-oriented n-type (10–20 Ω cm) silicon substrates were chemically cleaned and thermally oxidized in dry O$_2$ at 1050 °C in order to grow a 100 nm thick SiO$_2$ layer. The SiO$_2$ layer was lithographically patterned to form appropriate oxide windows. The SiO$_2$ windows were aligned with respect to the (110) crystalline direction to allow a fast preliminary alignment of the sample on the XY stage in the FIB chamber relative to the scan direction of the FIB. Subsequently, the samples were locally implanted by a digitally scanned 60 keV Co$^{++}$FIB with an ion current in the range of 5–20 pA. The corresponding mean penetration depth of the ions is about 53 nm. The cobalt ions were extracted from a liquid metal ion source operating with a Co$_{36}$Nd$_{64}$ alloy (melting point of 566 °C). Separation of the Co$^{++}$ from the other ion species coming from the source was done by means of an E X B-type mass filter in the FIB column (Canion 31Mplus, Orsay Physics) which allows the focusing of the Co$^{++}$ ion beam into a spot diameter of 20–50 nm. For the study of the conventional IBS of CoSi$_2$ NWs (phase separation through precipitation and wire ripening during thermal treatment) and their decay into chains of nanoparticles due to NW instabilities, the samples were implanted with high doses ($1 \times 10^{16}$–2 $\times 10^{17}$ cm$^{-2}$). To avoid defect accumulation and amorphization of Si during implantation the samples were annealed in the range of 420–450 °C. The implantation was done in a digital mode with a short pixel dwell time (<2 μs) and a long relaxation time of more than 100 μs (time between two exposures of the same pixel). Additionally, the scan direction of the FIB was varied relative to the chosen crystalline direction for the study of the stability of NW growth. Usually, the FIB writing direction was parallel to one of (110) directions on the Si surface which correspond to the energetically favored growth direction of the CoSi$_2$ nanocrystals. In order to investigate the influence of locally FIB induced radiation defects on the CoSi$_2$ NW growth, the samples were implanted at lower ion doses ($10^{14}$–$10^{16}$ cm$^{-2}$) at room temperature. Before the FIB implantation the rear side of these samples was covered with a 10 nm Co layer by thermal evaporation to achieve a high concentration of Co in the Si bulk and a supersaturation of Co during cooling down of the samples in the thermal treatment. It was assumed that the amount of Co atoms above the solubility limit will precipitate preferentially on CoSi$_2$ nanoparticles or on defects formed in the FIB trace. After FIB irradiation the samples were annealed by a two step thermal treatment (30 min at 600 °C and 60 min at 1000 °C in dry N$_2$ atmosphere). In order to improve the image contrast for scanning electron microscopy investigations of the NWs a short reactive ion etching in CF$_4$ for 20–40 s was carried out to remove the 15–20 nm thick silicon top layer covering the buried CoSi$_2$ nanostructures. As it is shown in Fig. 1(a) conventionally synthesized NWs have lengths of 10–20 μm and diameters of 100–150 nm in the case of FIB implantation along the chosen (110) direction. A small deviation of the FIB trace from this direction leads to a decay of the NW into shorter ones [Fig. 1(b)]. Larger angles of misalignment result the formation of chains of more or less prolonged CoSi$_2$ nanoparticles [Fig. 1(c)].

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A further reduction of the NW diameter can be expected by decreasing the concentration of cobalt atoms implanted in silicon at the same FIB spot. NWs synthesized at lower doses of $1 \times 10^{16} - 3 \times 10^{16}$ cm$^{-2}$ are not stable and decay into shorter NW fragments with a diameter of about 50 nm [Fig. 2(a)]. Moreover, because of the existence of the other $\{110\}$ crystalline directions crossing the FIB trace, there is a certain probability of spontaneous and self-aligned NW growth in these directions [Fig. 2(b)]. One of the possible reasons of this effect should be related to the well known $\{311\}$ defects in silicon induced during FIB implantation.\textsuperscript{16} It can be assumed that the generation of $\{311\}$ defects in the silicon crystal plays a crucial role in the CoSi$_2$ nanowire formation process. $\{311\}$ defects consist of excess Si interstitials coming from FIB induced point defects which rapidly agglomerate at the beginning of annealing (temperature ramp up).\textsuperscript{17} They are relatively stable at temperatures below 600 °C, at 800 °C they grow up to 150 nm in length via a few minutes forming stable dislocation loops and ejecting silicon interstitials. These defects are closed between two $\{311\}$ planes and are elongated in the $\langle 110 \rangle$ direction.\textsuperscript{18} From transmission electron microscopy (TEM) investigations it is known that after annealing at 800 °C the $\{311\}$ rodlike defects can also transform into similar ones embedded in $\{111\}$ habit planes and elongated in the $\langle 110 \rangle$ direction.\textsuperscript{19} During annealing the implanted and solved Co atoms diffuse and can be gettered in the $\{311\}$ defects. They react with silicon and form silicide precipitates along these defects, i.e., along the $\langle 110 \rangle$ direction which is the most preferable direction for the one-dimensional CoSi$_2$ crystalline structure growth. This process stabilizes the defect structure and hinders dissolution of the rodlike defects. Subsequent Oswald ripening of the silicide precipitates along this $\langle 110 \rangle$ direction leads to the formation and alignment of oblong initial CoSi$_2$ nanoparticles at the defect position. During further heating the solvated cobalt atoms are still available around the nanoparticles and diffuse to them promoting the growth of crystalline CoSi$_2$ NWs. This finally results the formation of some micrometer long NWs.

In order to prove this assumption, a high concentration of defects was introduced by FIB line implantation of Co$^+$ and Co$^{++}$ as well as of other ions (Nd$^{++}$, Ga$^+$, Au$^+$, and Si$^{++}$) at doses of $10^{14} - 10^{15}$ cm$^{-2}$ at room temperature. The samples were covered with a 10 nm Co film on the rear side. After the FIB irradiation these samples were annealed at 1000 °C for different times in N$_2$ ambient. The cobalt layer on the rear side serves as a reservoir of cobalt atoms during annealing. At this temperature the solubility and the diffusivity of Co in Si are $5 \times 10^{14}$ cm$^{-3}$ and $1 \times 10^{-2}$ cm$^2$ s$^{-1}$, respectively. Already after 10 min of annealing short (200–500 nm) and 10–30 nm thin NWs self-aligned along the $\langle 110 \rangle$ directions were observed independent on the kind of implanted ions [Fig. 3(a)]. This effect was also clearly seen in the case of a dotlike FIB implantation (without pixel overlapping). It is essential that at lower doses ($10^{14} - 10^{15}$ cm$^{-2}$) the NW growth occurs more effectively than at higher ones, presumably depending on the defect structure complexity. After 30 min annealing the wires reach several micrometers in length and 20–50 nm in diameter [Fig. 3(b)]. Similar results were obtained using, for example, Ga$^+$ FIB irradiation [Fig. 3(c)] and irradiation with the other ions (not shown here). It should be mentioned here that these NWs are very stable (e.g., for some hours at 1000 °C), but it is difficult to provide a better controlled growth of such nanowires because of the spontaneous nature of the defect generation.
In conclusion, conventional ion beam synthesis of CoSi$_2$ NWs using high dose FIB implantation and subsequent annealing was demonstrated. The growth stability of long NWs embedded in Si sensitively depends on the accuracy of FIB trace alignment relative to the preferred growth directions, namely, the in-plane $\langle 110 \rangle$ Si crystal directions. A small misalignment of the FIB trace of a few degrees leads to the decay of the CoSi$_2$ NWs into shorter parts and a larger deviation causes a chain of CoSi$_2$ nanoparticles. Furthermore, it was observed that the stability of continuous NW growth is reduced with lowering the implantation dose. The controlled alignment of silicide NW growth is hindered by FIB induced defects initiating a spontaneous CoSi$_2$ NW growth along other in-plane $\langle 110 \rangle$ Si crystal directions. In contrast to conventional ion beam synthesis of CoSi$_2$ NWs by high dose FIB implantation along a narrow trace, the defect induced and self-aligned NWs seem to be more stable.

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