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Direct growth of nickel disilicide nanocrystals in silicon dioxide films

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Nickel disilicide (NiSi$_2$) nanocrystals (NCs) have been grown in silicon-rich oxide (SiO$_x$) films ion implanted with nickel by annealing at 1100 °C. It was found that NiSi$_2$ NCs grew into well-defined single crystalline structures embedded in a SiO$_x$ matrix and were approximately spherical in shape. The size of NCs can be influenced by limiting either the Ni or excess Si concentration. It was found that the resulting NCs could be produced with diameters in the range from 5 to 40 nm in the SiO$_x$ layers with excess Si concentrations of 4–8 at. % implanted with Ni concentrations of 0.1–10 at. %, © 2006 American Institute of Physics. [DOI: 10.1063/1.2202740]

Semiconductor devices continue to shrink and many rely on quantum phenomena associated with electrons and atoms. Such devices require special fabrication technologies to reach their full potential and these often require different approaches to those employed in present microelectronics. For example, a single-electron quantum dot (QD) transistor, a device called a single-electron tunneling (SET) transistor, has attracted much attention.\textsuperscript{1-5} This device is based on an intrinsically quantum phenomenon: the tunnel effect. It exploits the quantized transfer of electrons through the insulating barrier between quantum dot and source/drain,\textsuperscript{6} as proposed in principle by Averin and Likharev.\textsuperscript{7} The sufficient conditions to operate a SET transistor are that the QD electron charging energy ($\varepsilon^2/2C$, where $\varepsilon$ is the charge of an electron and $C$ is the capacitance of QD) is higher than thermal fluctuation energy ($k_BT$, where $k_B$ is Boltzmann’s constant), and that the resistance of the insulator between QD and source/drain is larger than the quantum resistance ($\hbar/e^2$, where $\hbar$ is Planck’s constants). To make a SET QD transistor operate well at room temperature, the size of the quantum dot has to be smaller than 15 nm and embedded in a highly insulating material such as silicon dioxide. Here we report the direct growth of crystalline nickel disilicide (NiSi$_2$) nanocrystals (NCs) in silicon-rich silicon oxide (SiO$_x$) layers. We show that the NiSi$_2$ NCs grow into well-defined single crystalline structures embedded in a SiO$_x$ matrix, and that their size can be directly influenced by adjusting the concentrations of either silicon or nickel in a SiO$_x$ layer.

Nickel disilicide NCs were formed by thermally annealing Ni implanted silicon-rich silicon oxide (SiO$_x$) films. Thin (~200 nm) SiO$_x$ films of various Si concentrations were deposited on (100) CZochralski silicon wafers at a substrate temperature of 300 °C by plasma-enhanced chemical vapor deposition (PECVD) using a fixed flow rate of SiH$_4$ [160 SCCM (SCCM denotes cubic centimeter per minute at STP)] and a variable flow rate of NO$_2$ (75 SCCM for $x=1.70$, 50 SCCM for $x=1.56$, and 35 SCCM for $x=1.44$). The films were subsequently implanted with 130 keV Ni$^+$ ions, which resulted in a Ni concentration profile centered in the layer, with a peak ion concentration located at a depth of around 100 nm. The implant fluences were $6.0 \times 10^{14}$, $6.0 \times 10^{15}$, and $6.0 \times 10^{16}$ cm$^{-2}$, which nominally correspond to 0.1, 1.0, and 10.0 at. % Ni concentrations, respectively. The Ni concentration profile was confirmed by Rutherford backscattering spectroscopy (RBS) using 2.0 MeV He ions. Nucleation and growth of Ni disilicide NCs were achieved by annealing the Ni implanted SiO$_x$ samples at 1100 °C in a quartz-tube furnace using high purity nitrogen gas (99.999%) as an ambient. The microscopic structure of annealed SiO$_x$ layers and the size and crystallinity of NCs were studied by transmission electron microscopy (TEM) using a JEOL JEM 2010 instrument operating at 200 kV. The chemical composition of NCs was analyzed by energy dispersive x-ray spectroscopy (EDS) using an energy dispersive spectrometer attached to the TEM instrument. For the EDS analysis, the electron beam was focused to a spot as small as 1.5 nm in size.

Figures 1(a) and 1(b) show cross-sectional transmission electron micrographs (XTEM) of SiO$_x$ films ($x=1.56$) without and with 10 at. % Ni concentration, respectively, after annealing at 1100 °C for 4 h. It is seen that the Ni implanted SiO$_x$ layer contains a large number of NCs, while the unimplanted layer does not. The average size of the crystallites is larger at the middle of layer where the implanted Ni concentration reaches a maximum. This suggests that the formation of the NCs is related to the local concentration of Ni.

Figure 2 shows a high-magnification XTEM micrograph and associated electron diffraction pattern (inset) obtained from the SiO$_x$ layer shown in Fig. 1(b). The XTEM image shows the presence of NCs with well-defined boundaries and approximately spherical shape within the SiO$_x$ matrix. The detailed microstructure of the NC marked reveals a regular lattice structure consistent with it being a single crystal phase. This is confirmed by the electron diffraction pattern shown in the inset, which shows diffuse rings consistent with scattering from the amorphous SiO$_x$ matrix and discontinuous rings made up of individual diffraction spots, consistent

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with diffraction from a low concentration of randomly oriented crystallites.

The SiO$_x$ film used in Figs. 1(b) and 2 contains excess Si atoms ($x=1.56$) in addition to the implanted Ni. Annealing such silicon-rich silicon oxide films above 1000 °C generally produces Si nanocrystals\textsuperscript{8–10}. However, it is well known that Ni readily reacts with Si to form various Ni silicide phases, the exact phase depending on the ratio of Ni to Si and the annealing temperature\textsuperscript{11–15}. The NCs observed in the present samples are therefore likely to be either silicon or Ni silicide crystallites. Using the relation, $r_1/r_2=d_2/d_1=(h_1^2+k_1^2+l_1^2)^{1/2}/(h_2^2+k_2^2+l_2^2)^{1/2}$, where $r_1$ and $r_2$ are radii of two rings and $d_1$ and $d_2$ are the interplanar spacings of $(h_1k_1l_1)$ and $(h_2k_2l_2)$ planes corresponding to rings 1 and 2, respectively, we indexed the diffraction pattern shown in the inset in Fig. 2. This showed that the rings are consistent with the {111}, {200}, {220}, and {311} planes of NiSi$_2$.

Exact phase identification is, however, difficult from the electron diffraction patterns alone due to the small volume fraction of crystallites and the similarity between the lattice parameters of Si and various silicide phases (lattice constants both about 0.54 nm)\textsuperscript{16}. To assist in this regard energy dispersive EDS was performed on individual NCs. Figure 3 presents representative EDS spectra obtained from outside [Fig. 3(a)] and inside [Fig. 3(b)] a NC. The spectrum presented in Fig. 3(b) was obtained from a NC showing the highest Ni concentration within the field of view. Little, or no Ni is observed in the region between NCs. These qualitative EDS data demonstrate that NCs contain Si and Ni, supporting the premise that they are silicide crystallites. It should be noted, however, that EDS analysis on a range of NCs showed variations in the Ni:Si ratio, ranging from 1:9 up to about 1:2. At least part of this variation arises from the fact that the analysis volume includes regions outside the NC, despite the small lateral size (1.5 nm) of the electron beam.
There are many stable Ni silicide phases, depending on the annealing temperature, typically Ni$_2$Si, NiSi, and NiSi$_2$ form for annealing temperatures below 350, 350–750 °C, and above 750 °C, respectively. The NCs presented in the previous figures were formed by annealing at a temperature of 1100 °C, where the stable phase is expected to be nickel disilicide (NiSi$_2$). In addition, the EDS data show the presence of NCs with Ni concentrations of about 33 at. %, although it varied from NC to NC, similar to that expected in the NiSi$_2$ single crystal structure. These data provide strong support for the existence of NiSi$_2$ NCs.

Finally, nucleation and growth of NiSi$_2$ NCs in the Ni implanted SiO$_2$ layers are considered. The annealing-time dependence of NC size, which was obtained from a SiO$_2$ layer with $x=1.56$ (i.e., approximately 6 at. % excess Si) and 10 at. % Ni, as annealed at 1100 °C, is shown in Fig. 4(a). The Ni concentration dependence of NC size obtained from SiO$_2$ layers with a fixed concentration of Si ($x=1.56$) and the Si concentration dependence of NC size obtained from SiO$_2$ layers with a fixed concentration of Ni (10 at. %), which were annealed at 1100 °C for 4 h, are shown in Figs. 4(b) and 4(c), respectively. The filled squares represent the average NC diameters calculated for the NCs in each layer, while the bars represent the distribution (minimum-maximum) of diameters.

Figure 4(a) reveals that the average diameter of NCs is nearly independent of annealing time after 1 h. In a two-dimensional layer a spherical NiSi$_2$ particle is expected to grow according to a power law of the form $r \sim t^n$, where $r$ is the radius of the sphere, $t$ is annealing time, and $n$ has a typical value of 1/3. Since nucleation of NiSi$_2$ precipitates is expected to proceed rapidly at 1100 °C the constant NC size in the present case suggests that further growth is limited by the supply of Ni or Si.

Figure 4(b) shows that the average NC diameter increases with increasing Ni concentration after annealing for 4 h. This annealing time, as seen in Fig. 4(a), is sufficient for complete growth of the NCs. The size is also affected by the supply of Si, as shown in Fig. 4(c). In this case the diameter also increases with increasing Si concentration. These results suggest that the size of NiSi$_2$ NCs can be influenced by varying either the Si or Ni concentration in the SiO$_2$ layer.

In summary, it has been shown that NiSi$_2$ NCs can be formed in silicon-rich oxide layers containing ion-implanted Ni, and that the size of these NCs can be influenced by limiting either the Ni or excess Si concentration. The resulting NCs are approximately spherical in shape and can be produced with diameters in the range from 5 to 40 nm.

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