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# Fabrication of periodic nickel silicide nanodot arrays using nanosphere lithography

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**Abstract**

The interfacial reactions of the 2D-ordered nickel metal nanodots that were prepared by polystyrene nanosphere lithography (NSL) on Si substrates after different heat treatments have been investigated. Epitaxial $NiSi_2$ nanodot arrays were found to form at a temperature as low as 350 °C. The results indicated that the growth of epitaxial $NiSi_2$ is more favorable for the Ni metal dot array samples. The sizes of these epitaxial $NiSi_2$ nanodots in samples annealed at 350–800 °C are in the range of 84–110 nm. The shape of the epitaxial $NiSi_2$ nanodot was found to be pyramidal. Furthermore, for the samples annealed at 900 °C, amorphous $SiO_x$ nanowires were found to grow on individual nickel silicide nanoparticles. The diameters of these nanowires are in the range of 15–20 nm. As the size of metal nanodot can be adjusted by tuning the diameter of the polystyrene (PS) spheres, the NSL technique promises to be an effective patterning method without complex lithography.


*Keywords:* Nanosphere lithography; Epitaxy; Silicide nanodots; Nanowires

## 1. Introduction

For the applications of nanotechnology, the periodicity and size uniformity of produced nanomaterials are two major challenges. Well-ordered nanostructures have already been found their potential applications in advanced optoelectronic devices, biosensors, and data storage [1,2]. To fabricate large-area, periodic nanodot arrays, various nanoscale fabrication techniques such as scanning probe lithography, electron beam and X-ray lithography have been developed [3,4]. However, the high cost and serial processing format of these techniques may limit their utilities. Therefore, many recent research efforts have been devoted to the development of low-cost, high-throughput lithography techniques, which are based on self-assembled processes. Among these approaches, an effective and economical technique–nanosphere lithography (NSL)–is one of the most promising schemes to replace the conventional lithography methods. In this technique, a series of polystyrene (PS) spheres of different diameters are self-assembled onto substrate surfaces. These periodic nanosphere structures can be used as a template to fabricate nanostructure arrays without complex lithography.

Recently, many two-dimensional (2D) well-ordered arrays of metal nanoparticles have been successfully formed on Si substrates by the PS sphere lithography [5–7]. The 2D ordered metal nanodots can be subsequently used as catalysts to grow well-aligned nanowire or nanotube arrays under different heating conditions [8,9]. However, studies of interfacial reactions of these metal nanodots on Si substrates after different heat treatments are extremely rare. In addition, in applications of future nanodevices, the reactions between metal thin films and Si substrates are restricted to laterally confined nanoscale areas. Previous studies showed that the reduction of linewidth highly influences the growth and phase transformation of metal silicides [10–12]. Recently, studies of nickel silicide formation have gotten much attention, because the low-resistivity nickel monosilicide (NiSi) is perhaps the most promising candidate for nanometer-scale device contact

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materials [13,14]. Therefore, it is of much interest to precisely investigate the interfacial reactions of Ni metal dots on Si substrates taking advantage of the PS NSL techniques to define the large-area periodic nanodot structures.

In the present study, results from an investigation on the formation of 2D-ordered nickel metal dot arrays and phase transformations of the nickel metal dots on (001)Si substrates after annealing at different temperatures are reported.

## 2. Experimental procedures

To fabricate the nanosphere lithography masks on Si substrates, suspensions of 600-nm-diameter monodispersed polystyrene spheres and 1 cm × 1 cm single-crystal, 10–20 Ω cm, boron-doped (001)Si substrates were used in the present study. The PS suspensions were diluted in a solution of the surfactant Sodium Dodecylsulfate (SDS). The concentrations of PS spheres and the surfactant SDS in this mixed solution were 1.2 wt.% and 0.01 wt.%, respectively. The 1 cm × 1 cm Si substrates were cleaned by a standard process and then dipped in a dilute HF solution ($HF:H_2O$:1:50) before the drop-cast process. A 25-μL droplet of the prepared PS suspensions was drop-cast with a pipette on the surface of a clean Si substrate. The solvent was evaporated while placing the substrates in a custom-built humidity controlled apparatus. The samples were sonicated during drying to obtain a monolayer with large highly ordered areas.

A 20-nm-thick nickel thin film was deposited onto the polystyrene masks at room temperature. The base pressure in the evaporation chamber was better than $1 \times 10^{-5}$ Pa. The deposition rate was about 0.04–0.05 nm/s. After Ni thin films deposition and subsequent lift-off of the PS spheres using Methyl Ethyl Ketone (MEK) solutions, an ordered hexagonal Ni nanodot array was formed on the Si substrate. Heat treatments were carried out in a three-zone diffusion furnace at 350–900 °C for 30 min in $N_2$ ambient.

Scanning electron microscopy (SEM) was utilized to examine the periodicity and surface morphology of the self-assembled PS sphere masks and the metal nanodot arrays. Transmission electron microscope (TEM) in conjunction with an energy dispersion spectrometer (EDS) was carried out for phase identification and chemical composition determination. High-resolution TEM (HRTEM) was used to investigate the interfacial atomic structures between Ni silicide nanodots and Si substrates. Most of the cross-sectional TEM (XTEM) micrographs were taken along the [110] zone axis of single-crystal Si.

## 3. Results and discussion

From SEM observation, a hexagonally close-packed monolayer of PS spheres was found to form in drop-cast samples by self-assembling under appropriate concentration and humidity. An example is shown in Fig. 1. A few point defects and stacking faults were observed in some regions of the monolayer of PS spheres (indicated by arrows in Fig. 1). The irregular features are essentially due to the dispersion of the diameter of the PS spheres. However, the defect-free regions are large enough for the purpose of this study. The perfectly ordered PS sphere array is shown as the insert of Fig. 1. These self-assembled arrays of PS spheres were then used as a mask for the deposition of Ni thin films. The Ni particles were only deposited onto the triangular-shaped areas of Si substrates which were not shadowed by the PS sphere masks. Fig. 2 shows SEM images of the well-ordered array of triangular Ni dots formed on the surface of Si substrate after the lift-off of the PS spheres.

For these samples annealed at 350–800 °C, large-area, 2D-ordered nickel silicide nanodot arrays were formed on Si substrates. An example is shown in Fig. 3. The sizes of the silicide nanodots were found to decrease with annealing temperature. From planview TEM observation and selected area electron diffraction (SAED) analysis, epitaxial $NiSi_2$ was found to form in all samples annealed at 350–800 °C. The sizes of these epitaxial $NiSi_2$ nanodots are in the range of 84–110 nm. From (200) dark-field TEM micrograph of annealed samples, only $NiSi_2$ nanodots were observed (bright contrast). The results indicated that the {200} diffraction spots correspond to the epitaxial $NiSi_2$ phase. The TEM bright-field images and (200)$NiSi_2$ dark-field images of samples annealed at 350 °C are shown in Fig. 3(b) and (c), respectively. The rugged contrast in the TEM image of the epitaxial $NiSi_2$ nanodots could be attributed to the existence of faceted structures and interfacial dislocations. Similar contrast phenomena of epitaxial silicides were also observed in previous studies [15–18]. In addition, the orientation relationships of epitaxial $NiSi_2$ nanodots with respect to (001)Si substrates were identified to be [001] $NiSi_2$//[001] Si and (200) $NiSi_2$//(400) Si. The corresponding electron diffraction pattern is shown in Fig. 3(d). Similar results were found in the other annealed samples. With closer examinations, many of the epitaxial $NiSi_2$ nanodots

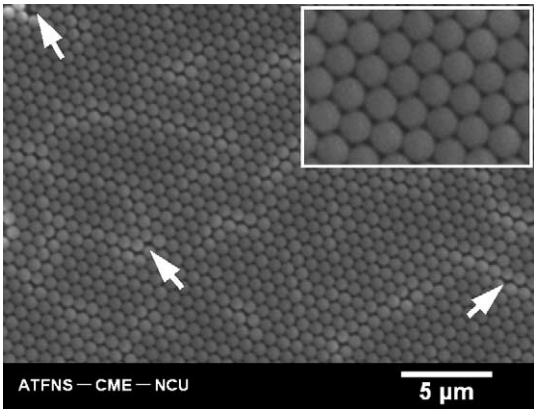


Fig. 1. The SEM image of a self-assembled monolayer of PS spheres on Si substrate. The inset is a magnified view of the selected region of the PS sphere array.