Low Temperature Nickel Induced Crystallization of Amorphous Silicon Nanorods on Silicon and Glass Substrates

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Abstract: In this work, crystallization of amorphous silicon (a-Si) nanorods was done by metal induced crystallization (MIC) method at low temperature (500°C) suitable for circuit applications and low cost, disposable biosensors. The crystallization of a-Si nanorods was investigated by Raman and TEM methods. These data showed oriented crystallized Si nanorods have been obtained by metal induced crystallization (MIC) method on different substrates, which can be suitable for 3D integrated circuits, optical and electrochemical applications. This simple method can be used to produce silicon nanorod arrays with high quality suitable for nanoelectronic and optoelectronic applications.

Keywords: Metal Induced Crystallization (MIC); Amorphous Silicon (a-Si) nanorods; 3D integrated circuits.

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1. Introduction

In recent years ordered silicon nanorods have received extensive interest due to their attractive applications as building blocks for advanced electronic devices such as transistors [1], optoelectronic devices [2,3], biosensors [4] as well as energy devices such as battery and solar cells [5-9]. As in many applications of silicon nanorod arrays, it is important not only to control the regularity and uniformity in terms of diameters and length but also to adjust crystalline phases.

Microelectronic and nanoelectronic devices of the future will require quasi-one-dimensional semiconductors with nanoscale size and ordered arrays and at the same time with single crystal structure [10]. For example, fabrication of single crystalline vertically aligned silicon nanowires at low temperature is outmost important to design of 3D integrated circuits (3D-ICs) [11,12] because of the facility of charge mobility. However, conventional method for crystallization of silicon is thermal annealing [13]. This process needs a long time and high temperature, which is not desirable for efficient manufacturing. Alternative process has been included laser annealing and metal-induced crystallization [14, 15].

Laser annealing is fast but suffers from poor uniformity and narrow process window [14]. In comparison, metal-induced crystallization methods have been proposed to shorten the annealing time and lower the process temperature [15, 16].

Between several metals, which are used for metal-induced crystallization such as Ni, Pd, Al,
nickel induces lower defects on silicon [17]. Also in many applications crucial parameter is good electrical and mechanical contact between active material (silicon nanostructure) and substrate and each application need specific substrate. So if we can generate ordered silicon nanorods on a different substrate, these structures will be useful for wide range of applications.

For example, silicon nanorods on SiO$_2$ can be suitable for 3D integrated circuits because SiO$_2$ layer acts as isolating layer between transistors. Using metal substrate such as Cr and Ni, can be desirable for biosensor and battery applications and glass substrate can be used as optoelectronic devices. So, possibility of vertically aligned crystalline silicon nanowires fabrication with good contact to the substrate and high uniformity with low temperature crystalline process is one of the most important steps to get the most of these unique structure in the wide range. As a result, in this work we have proposed a method to achieve this aim. We have deposited amorphous silicon on different substrates (SiO$_2$, Cr, Ni, glass). And then, silicon nanorods have been fabricated using Reactive Ion Etching (RIE) and NanoSphere Lithography (NSL) methods in large area. After that, amorphous silicon nanorods were converted to near single crystal vertically aligned silicon nanowires through metal-induced crystallization method at low temperature.

In this method, nickel mask acts as RIE mask and crystallization seed simultaneously.

2. Materials and Methods

The fabrication process includes five steps: (1) 800 nm thick a-Si film was deposited on a Si/SiO$_2$ substrate by a Unaxis 790 radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) unit operated at 13.56 MHz. The substrates temperature was set at 300°C, heated from the bottom of them via a ceramic heater.

The pressure and power density were set at 1 torr and 0.25 W/cm$^2$, respectively. A mixture of SiH$_4$ and H$_2$ gases with respective flow rates of 16 and 80 sccm was used as the source gas. The substrate size used in our work was 1 cm $\times$ 1 cm, although the processing of larger substrates is feasible. (2) the amorphous silicon was coated with 460 nm polystyrene (PS) spheres through spin coating to form an ordered structure on the a-Si thin film surface; In order to create a hydrophilic surface on a-Si film to facilitate self-assembly of the nanospheres, amorphous silicon surface had been passivated with O$_2$/H$_2$ plasma for 5 s in RIE before nanosphere spin coating. (3) 8 nm thick nickel film was electron-beam evaporated on the nanospheres and filled the free space between them.

Lifting-off the polystyrene beads through sonication in dichloromethane solution for four minutes, nickel nanostructures in ordered arrays were remained on a-Si surface to act as a hard-mask for subsequent etching purposes. (4) After liftoff of polystyrene, we etched the sample using hydrogen assisted deep reactive ion etching method to produce the amorphous silicon pillar array with the width and height of around 100 and 800 nm, respectively. The sample was placed in an RIE chamber and etched with SF$_6$ plasma.

Etch conditions were as follow: Etching process uses SF$_6$ with flow of 40 sccm, plasma power of 130 W and 8 s duration in around 160 mTorr in the etching step. For the passivation step, a gas mixture of O$_2$/SF$_6$/H$_2$ with respective flows of 230/4/620 sccm was used for a period of 50 seconds and plasma power of 210W in the pressure of 600 mTorr. This high-precision RIE method for fabrication of amorphous silicon nanorod array was explained in detail in our previous works [my apl and jnm].

A Hitachi S4160 scanning electron microscope (SEM) was used to characterize the morphologies of the Silicon film and nanorods. (5) Then we tried to crystallize our nanorods at low temperature compatible with commercial applications. Nickels, which were used as masks of etching in the previous step, can act as seeds of metal induced crystallization of amorphous silicon nanorods.

The crystallization was characterized using Raman spectroscopy and Transmission Electron Microscopy (TEM). Raman spectra were obtained by a Bruker Senterra Raman spectrometer equipped with 785nm LASER diodes.

Also, a Philips CM300 transmission electron microscope (TEM) was used to probe the crystallinity of the silicon nanorods after annealing.
3.1. a-Si nanorod arrays

Cross sectional scanning electron microscopy (SEM) image of amorphous silicon film deposited on SiO$_2$/Si is shown in figure 1(a). The image verifies the deposited a-Si has a smooth surface and suggests that there is strong adhesive contact between deposited a-Si and the substrates as there are no visible defects seen at the film/substrate interface. Therefore, this layer can be used for nanosphere lithography. Using NSL and hydrogen assisted DRIE, a-Si nanorod arrays were formed as shown in figure 1(b). Depending on the number of nanosphere layers on the surface the pattern of ordered arrays can be different (figure 1(b,c)). Finally, the transmission electron microscopy (TEM) image of a fabricated a-Si nanorod in part (d) demonstrates the amorphous nature of the nanorods after the process completion, which is also confirmed by the electron diffraction pattern in the inset of this image.

![Figure 1](image)

**Figure 1.** SEM images of (a) amorphous silicon film deposited Si/SiO$_2$, indicating a smooth surface. (b,c) Tilted views of highly ordered vertical features of amorphous silicon nanorods formed by nanosphere lithography and vertical etching in RIE on Si/SiO$_2$ and glass substrates, respectively. Inset of b shows the monolayer of nanospheres placed on a-Si through spin coating. (d) Transmission electron microscopy (TEM) image and selected area diffraction (SAD) pattern of an a-Si nanorod.

3.2. Ni induced crystallization of a-Si nanorods.

Traditionally, metal-induced crystallization (MIC) method has been utilized to crystallize a-Si film at low temperature [15-17]. But the crystallized film is usually polycrystalline with longitudinal grains along the lateral crystallization direction [18]. By patterning the a-Si film and fabricating vertical nanorods before the crystallization, however, we found that near single crystal Si can be achieved.

Metal induced crystallization of a-Si nanorods was occurred by nickel seeds. Heat treatment was done in a conventional atmospheric pressure horizontal furnace under N$_2$ environment at different temperatures for 2 hours. The samples...
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after annealing are studied by Raman and TEM to see the crystallization of a-Si nanorods.

Room temperature Raman spectra of silicon nanowires before and after annealing are presented in figure 2(a). The crystalline fraction of the samples were evaluated from the Raman spectra in Raman frequency range from 300 cm\(^{-1}\) to 700 cm\(^{-1}\) where the amorphous-to-crystalline transition had been observed as a change of a transverse optical (TO) phonon mode. It is well known that the Raman spectra of partially crystallized amorphous silicon, a mixed phase of both amorphous and crystalline, have two peaks at least; one is strong band peak around 520 cm\(^{-1}\) and the other is broad band peak centered at 480 cm\(^{-1}\), which are due to the TO modes for crystalline and amorphous phases, respectively [18]. Figure 2(a) shows the spectrum of silicon nanowires before and after 450°C, 480°C and 500°C heat treatment for 2 hours. The broad structure near 480 cm\(^{-1}\) in the spectrum indicates amorphous silicon which gradually shrinks by annealing temperature and finally disappeared after 500 °C heat treatment. Sharp peak at 521 cm\(^{-1}\) was detected in the spectrum of silicon nanowires after heat treatment at 500 °C, indicating the a-Si has been totally crystallized.

Figure 2. The Raman spectrum of silicon nanowires (a) with nickel before and after 450°C, 480°C and 500°C heat treatment (b) after 500°C heat treatment with and without nickel.

To confirm that nickel acts as crystallization seeds of silicon nanorods we have compared Raman spectra of silicon nanorods with and without nickel existence (figure 2(b)). It can be obviously seen that without nickel silicon nanorods cannot be crystallized. As figure 2(b) indicates, the a-Si rods without Ni remained amorphous even after 10 hours annealing at 500 °C.

Figure 3. (a) Dark field and (b) bright field TEM images of silicon nanorods with different diameters after 30-minute annealing at 500°C.

It is worthy to note that the samples for Raman were prepared on glass substrates (not on Si/SiO\(_2\) substrates) to ensure that crystalline silicon peaks are only due to the crystallization of amorphous silicon nanorods and not attributed to substrate. TEM was applied to evaluate the effect of Si nanowires size on crystallization. It can be seen that after 30-minute annealing at 500°C Ni atoms diffuse

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toward a-Si and during the nickel silicide diffusion the size of crystallized grain increases making the nanowire near single crystal silicon (Fig 3a). For comparison, the a-Si nanowire with nickel mask and the diameter of more than 200 nm was again annealed at 500°C and the a-Si nanowire became polycrystalline as the grain size was not large enough to make the whole nanowire single crystal (Fig 3b). The inset shows a selected area diffraction pattern of crystallized nanorod.

4. Conclusions

Low temperature crystallization of amorphous silicon (a-Si) nanorods was successfully done by metal induced crystallization (MIC) method on different substrates suitable for various applications. Raman and TEM methods were employed to investigate the crystallization of nanorods and it was confirmed that nickel nanoparticles could act as both masks and crystallization seeds. This method can pave a new way to produce silicon nanorod arrays with high quality suitable for nanoelectronic and optoelectronic applications.

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Conflicts of Interest

The authors declare no conflict of interest.

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