NeoSilicon materials and silicon nanodevices

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Abstract

We propose a novel material NeoSilicon, in which both particle size and interparticle distance of nanocrystalline silicon (nc-Si) quantum dots are precisely controlled. New functions in electron transport, photon emission and electron emission are expected due to quantum effects at room temperature and large interaction between dots. The bandgap is determined by the particle size. The conductivity is controlled mainly by tunneling processes. The transport characteristics are also controlled by charge quantization effect. We present fabrication and characterization of NeoSilicon. Based on the idea of separation of the nucleation and the growth processes in plasma decomposition of silane, we have successfully prepared nc-Si particles of 8 nm in diameter with size dispersion of 1 nm, whose surfaces are covered by naturally formed oxide of 1.5 nm thickness. Further reduction of dot size is achieved to 4 nm using self-limiting oxidation processes. Single electron transport characteristics of nc-Si are demonstrated in both planar and vertical transistor structures. Highly efficient electron emission is observed in NeoSilicon samples. Photoluminescence intensity enhancement due to no-phonon-assisted indirect transition is observed in strongly confined nc-Si dots covered by oxide.

Keywords: Nanostructures; Silicon; Single electron tunneling; Ballistic transport; Electron emission; Photoluminescence

1. Introduction

NeoSilicon, a novel man-made material, is proposed. In NeoSilicon, both particle size and interparticle distance of nanocrystalline silicon (nc-Si) quantum dots are precisely controlled. New functions in electron transport, photon emission and electron emission are expected due to quantum effects at room temperature and large interaction between dots. The bandgap is determined by the particle size. The conductivity is controlled mainly by tunnel barrier height and thickness. The transport characteristics are also affected by the charge quantization effect.

NeoSilicon is expected to be widely applicable to the key devices in electronics, including ultra-large-scale-integrated circuits and display devices. Enlarged bandgap of NeoSilicon allows fabrication of ultra-low leakage current MOS transistors while keeping high operating speed of current Si integrated devices. Moreover, new field in electronics by using single electron devices, light-emitting diodes, laser diodes, electron-
parent between grains, the precise control of grain size is difficult. Porous Si has high controllability in dot size, but interaction between dots is small. Described here are surface-oxidized nanocrystalline Si dots, which have high controllability in both particle size and interparticle distance.

2. Preparation of NeoSilicon

Fig. 1 shows the nc-Si fabrication system, which consist of an UHV chamber equipped with a plasma cell, a sample exchange chamber and an oxidation chamber. nc-Si is formed by very high-frequency plasma decomposition of silane [8] and coalescence of radicals. The wall of the plasma cell is heated to 100 °C so as to avoid deposition of polysilanes. Silicon fine particles formed in the plasma cell are extracted through an orifice to the UHV chamber and deposited onto various substrates at room temperature. Fig. 2 shows high-resolution TEM image of an nc-Si dot with spherical shape. The lattice image clarifies that the ultra-fine particle is a single-domain crystal. The surface of nc-Si is covered by natural oxide of 1.5 nm thickness. It is notable that in this condition of low discharge plasma of silane, an amorphous silicon film is deposited onto a low-temperature (100 °C) substrate placed in the plasma cell. However, single crystalline particles are formed in the free space, where it is hot enough for crystallization and no quenching effect takes place. We evacuated the base pressure of the UHV chamber to $10^{-10}$ Torr, in order to avoid spurious effects due to impurity atoms. The pressures in the plasma cell and the UHV chamber during deposition are 0.4 Torr and 1 mTorr, respectively. In this case, since the mean free path of silane-derived radicals is much shorter than the distance between the orifice and the substrate, amorphous silicon is not deposited on the substrate. Single domain crystalline dots are formed. Since the starting
material contains hydrogen, the surface dangling bonds of the nc-Si particles are always terminated by hydrogen atoms during growth processes. This surface structure guarantees the controlled growth of nc-Si. Only selected surface reaction between radicals and S–H bond contributes for the growth. The surfaces of as-deposited nc-Si dots are covered by hydrogen. However, after exposure to the air, the surface of nc-Si is naturally oxidized even at room temperature as shown in Fig. 2. Serving as a potential barrier layer, which controls electron confinement and electron transport, quality of the surface oxide layer is very important. The fabrication system has an oxidation chamber, which allows controlled oxidation before exposing the nc-Si dots to the air atmosphere.

The basic idea for the formation of uniform size nc-Si is separation of the nucleation and the crystal growth processes as shown in Fig. 3. If we could control the growth period constant, we should have uniform dot size. We found that hydrogen dilution of SiH₄ enhanced the nucleation rate significantly. We have introduced hydrogen gas pulse into the SiH₄ plasma, in which nucleation of nc-Si particles takes place. During the off state of hydrogen gas supply, radicals formed by plasma decomposition of SiH₄ tend to contribute to grow already nucleated particles rather than to create new nuclei. The next hydrogen gas pulse forces nc-Si particles grown in the previous cycle out of the plasma cell into the deposition chamber and the next nucleation of nc-Si occurs simultaneously. Fig. 4 shows size distribution of nc-Si prepared by (a) 100% SiH₄ gas and (b) pulsed H₂ gas inserted in SiH₄ plasma. When pulsed gas was applied, monodispersed particles of nc-Si with average size of 8 nm and dispersion of 1 nm have been obtained [9,10]. We have also found that argon dilution markedly enhances the deposition rate of nc-Si, due to the more efficient plasma activation by heavier argon ions [11]. By increasing number of cycles of gas pulses, we can increase the dot density per area and even we can deposit a multi-layered stack of Si particles. As shown in Fig. 5, we obtained an array of nc-Si dots with almost uniform diameter and surface oxide thickness.

![Fig. 3. Nucleation and growth processes of nc-Si [10].](image1)

![Fig. 4. Particle size distribution of nc-Si (a) without and (b) with pulsed gas supply [10].](image2)

![Fig. 5. TEM image of surface-oxidized nc-Si dots.](image3)
3. Electron transport

In order to investigate electron transport characteristics of nc-Si, we prepared transistor structure both in planar and vertical configurations. We fabricated very narrow (15 nm) gap source–drain electrodes by electron beam lithography and electron cyclotron resonance reactive ion etching of doped silicon-on-insulator wafers. We deposited nc-Si dots on top of the narrow electrodes followed by oxide barrier layer formation. The planar device was completed by deposition of gate oxide and gate electrode formation. The array of surface-oxidized nc-Si serves as a channel of the transistor. Since the size of tunnel junction was small enough, single electron transport characteristics such as Coulomb oscillation was obtained as shown in Fig. 6 [12]. Measurement and analysis of transport characteristics of devices with various inter-electrode distances and temperatures allowed modeling of transport in a single quantum dot and interaction between dots. Coulomb oscillation was also observed at room temperature.

The vertical transistor with wrap-around gate was prepared by drilling EB-defined hole in multiple layers of oxide and polysilicon using various mode of etching and deposition of nc-Si dots followed by CVD of polysilicon [13]. Periodic current oscillation with varying gate voltage, as shown in Fig. 7, is an evidence of single electron tunneling in surface-oxidized nc-Si. The presence of more than two frequency of the oscillation is due to the effect of multiple junctions caused by the neighboring dots. In order to verify that the Coulomb oscillation is really due to a surface-oxidized nc-Si dot, we prepared a vertical transistor without dot deposition. The current level was markedly different. Moreover, we found quantized conductance due to ballistic transport [14,15], since the gate length of 20 nm, defined by the thickness of CVD polysilicon, was much shorter than the electron mean free path of Si and the width of the channel could be confined by applying field to the wrap-around gate electrode.

We have also studied single electron memory devices with nc-Si dots as floating gate [16]. Some recent results are shown in this issue [17].

4. Electron emission

Highly efficient electron emission was observed from multiple layers of nc-Si dots array [18]. Based on the advantage of high efficiency, low-voltage operation, pressure insensitivity and small-angle dispersion, surface-emitting cold cathodes are promising for applications in flat-panel displays, electron gun arrays and microwave tubes. Although porous silicon and porous polysilicon diodes fabricated by electrochemical etching and oxidation are extensively studied [6,7,19], we demonstrated nc-Si dots prepared by dry processes were also promising [18]. A sample consisting of multiple layers of nc-Si dots array was deposited on a Si wafer, surface-oxidized and topped by a very thin layer of Au. When applied bias between Au and Si substrates exceeds the work function of Au, 5 V, the electron emission takes place and collected by a collector plate located 5 mm apart from the Au electrode. Typical diode and emission current characteristics are shown in Fig. 8. The mechanism of high-efficiency electron emission is due to ballistic transport in nc-Si [19]. Planarization heat treatment causes the reduction of voids between dots and enhances electron emission efficiency to 4.5% [18].

5. Photoluminescence

Surface-oxidized nc-Si shows visible photoluminescence. PL measurement was performed at room temperature with the 325 nm line from a He–Cd laser excitation. Fig. 9 shows the PL spectra for nc-Si samples.
with various dot sizes, which are prepared by controlling the oxidation time [20]. The PL spectrum of each sample can be deconvoluted into three Gaussian curves. P3 is not related to nc-Si dots and may be due to oxide. P1 may be due to interface states between nc-Si and oxide. Since P2 shows strong blue shift with decreasing dot size, this emission is associated with nc-Si dots. It is notable that the peak intensity of P2 increases with decreasing dot size. This phenomenon can be explained by taking into account that the no-phonon-assisted indirect transition in nc-Si is enhanced when dot size becomes less than the exciton Bohr radius of Si and strong confinement of electrons takes place. This result is very promising for optoelectronic application of nc-Si.

6. Summary

NeoSilicon, a novel quantum functional material, is proposed. Fabrication of NeoSilicon based on plasma decomposition of silane, separation of the nucleation and the growth processes for uniform size distribution, and self-limiting oxidation for high-quality potential barrier formation are described. Single electron transport characteristics of nc-Si are demonstrated in both planar and vertical transistor structures. Highly efficient electron emission is observed in NeoSilicon samples. Photoluminescence intensity enhancement due to no-phonon-assisted indirect transition is observed in strongly confined nc-Si.

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References