Aligned 1D silicon nanostructure arrays by plasma etching

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Abstract

High-density aligned arrays made of one-dimensional (1D) silicon nanostructures, including nanocone, nanorod, and nanowire, are fabricated by plasma etching in a hot-filament chemical vapor deposition apparatus using the gas mixture of hydrogen, nitrogen and methane. The silicon nanocones are crystalline structure and have a uniform apex angle of about 22°. The cones can be coated in situ with an about 3 nm thick amorphous carbon film by increasing the methane concentration in source gases. With gradually decreasing the plasma intensity, the morphologies of the silicon nanostructures evolve along the nanocone–nanorod–nanowire route, and the nanowire becomes amorphous structure. The model for fabrication process of silicon nanostructures with different morphologies will also be suggested.

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1. Introduction

Aligned one-dimensional (1D) silicon nanostructure arrays are of great interest due to a wide variety of applications in vacuum microelectronic and optoelectronic devices, flat panel displays [1] and semiconductor field emitting [2–4]. As a field emitter array, silicon tips are required to be small in size and uniformly distributed, and have high density at large scale. Lithographical technique is normally employed to produce silicon tip arrays, by which the tips with small sizes, even below 10 nm in diameter, can be obtained [5,6] although the fabrication process is expensive. Nanoscale silicon cones covering a large surface area can be prepared by using metal films as the plasma etching mask [7,8], but the heights and apex angles of the cones have a wide distribution. The microsize silicon tips are usually obtained by traditional methods of vapor–liquid–solid (VLS) growth process and chemical etching. It is, therefore, still a challenge to produce cost-effective nanosize silicon tip arrays for practical applications.

Much effort has been devoted to coating silicon cone arrays in order to improve their field emission properties. Evtukh et al. [9] made the silicon tip arrays coated with nanocomposite films. Wong et al. [10] fabricated the silicon cone arrays with cesium coating. Nagao et al. [11] deposited NbN, thin film on the silicon cone arrays. Many other researchers have also studied the effect of diamond coating on silicon tip arrays [12–14]. But for all of these approaches, the thickness of the coating layer is rather difficult to control, which is important in determining their field emission properties.

In this paper, high-density uniform arrays of 1D silicon nanostructures, including nanocones, nanorod, and nanowire, have been fabricated by a plasma etching process in a hot-filament chemical deposition (HFCVD) apparatus. By increasing methane concentration in the source gases, the silicon nanocones are coated in situ by thin amorphous carbon film, which is useful for their field emission application. With decreasing the plasma intensity, morphologies of the silicon nanostructures evolved from nanocone to nanorod, and then to nanowire. The growth process will be suggested.

2. Experimental

The aligned 1D silicon nanostructure arrays are fabricated on the HFCVD system. A dc power supply (630 V×1 A) was used to generate discharge plasma between the tantalum base (cathode) and a tantalum plate installed above a deeply carbonized tungsten filament (φ=0.3 mm). Polished Si (100) wafers (10 mm×10 mm) were used as substrates. The filament was heated to about
A negative bias in the range of 600–400 V were applied to generate a plasma of about 30–16 mA/cm² in intensity. The filament was used to assist dissociation of the inlet gases and generation of the plasma, which plays a key role in the sputtering of silicon substrate and re-deposition of the silicon atoms. The substrate temperature was maintained at about 900 °C. A mixture of hydrogen (99.999% purity), nitrogen (99.999% purity) and methane (99.9% purity) were used as the source gas. The gas flow rate was 100 sccm and the work pressure was kept at 4.0 kPa during the entire growth process (1 h). The flow rate ratio between hydrogen and nitrogen were kept at 3:1. The concentration (vol%) of methane was changed from 10 to 3% for the fabrication of silicon tips with and without in situ carbon coating, respectively. The morphology of the as-synthesized films was characterized by scanning electron microscopy (SEM). The microstructure and chemical compositions of the samples were determined by high-resolution transmission electron microscopy (TEM) and the energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS).

3. Results and discussion

3.1. Silicon nanocone arrays

A bias of 600 V and the 3 vol% concentration of methane were applied. The plasma intensity was about 30 mA/cm². The silicon wafer surface became dark grey after 1 h plasma etching. Fig. 1(a) is a top-viewed SEM image of a sample, the projected shape of the nanostructure is circular. Fig. 1(b) is SEM image viewed tilted 30° angle from its normal, showing a large-area silicon nanocone array. The cones are very uniform in both height and apex angle. The distribution of the cones is also uniform. The density of the cones is estimated to be about 10⁸/cm², which is one to two orders of magnitude higher than that reported previously [15]. The detailed information of the nanocones can be examined through high-magnification SEM image, as shown in Fig. 1(c). The tips are 400–500 nm in height and the average apex angle of the cones are ~22° after making the correction of the 30° view angle with the substrate normal. The diameters at the bottom of the cones are 200–300 nm. In the area of wider separations among cones, as indicated by arrowheads, the cone-shaped tips grow on well-aligned cylindrical pillars, which is a distinctive feature of our sample. This kind of nanocones may also serve as the tips for scanning probe microscopy.

The characterization of silicon nanocones by TEM is shown in Fig. 2(a). The selected area electron diffraction pattern, inset in Fig. 2(a), reveals that the tips are single crystalline with diamond structure. The apex angle as viewing along [111] is measured to be 22 ± 1°, in agreement with the measured apex angle by SEM image. Fig. 2(b) is an EDS spectrum of the nanotip, which further confirms that the sample is pure silicon.

By increasing the methane concentration in precursor to 10 vol%, the nanocone arrays, with similar density and uniformity as those shown in Fig. 1, can also be fabricated. The most interesting feature is that there is a thin and uniform film of carbon directly deposited onto the nanocone surface, as presented in Fig. 3(a). The high-resolution TEM image from the edge of the cone (circled in Fig. 3(a)) is shown in Fig. 3(b), which indicates that the silicon cone is coated by ~3 nm thick

Fig. 1. (a) Top-viewed SEM image of the as-prepared silicon nanocone array. (b) SEM image recorded at 30° angle from the substrate normal, showing the structural uniformity in size, apex angle and distribution. (c) A high-magnification SEM image.
amorphous film. Nanoprobe EELS was used to analyze the composition of the passivation layer on the nanocone. As shown in Fig. 3(c), there is a clear C k-edge peak, and no obvious Si peak was detected. We have also extended the EELS energy scope, there is no indication the presence of oxygen. Therefore, the coating is amorphous carbon film. The carbon-coated silicon nanocone arrays are promising for their application in field emission panel displays.

3.2. Silicon nanorod arrays

The bias was adjusted to 500 V, its corresponding plasma intensity was about 21 mA/cm². The other parameters were
same as those for fabrication of silicon nanocone arrays. The as-prepared products are aligned silicon nanorod arrays, as shown in Fig. 4(a). Fig. 4(b) is SEM image viewed from the peeled edge. Different from the above taper-shaped nanocones, the rods look much like tetrahedral cone shape, and have higher aspect ration, so we call them nanorods. From Fig. 4(b), it was estimated that the nanorods were about 1.5 μm in length. The fallen and broken nanorods along the peeled edge is a result of the peeling operation.

### 3.3. Silicon nanowire arrays

When the bias was decreased to 400 V, corresponding plasma intensity of 16 mA/cm², the morphology of the product also changed, as presented in Fig. 5(a), the silicon nanowire arrays were fabricated. Fig. 5(b) is TEM image of one nanowire. From the selected area diffraction pattern (Fig. 5(c)), the nanowires are amorphous structure. Fig. 5(d) is its EDS spectrum, which indicates the nanowire consists of several percent of carbon and oxygen.

### 3.4. Model for fabrication process

The fabrication of aligned silicon nanostructure arrays could be resulted from plasma etching together with re-deposition of silicon. Fig. 6 suggests the role of plasma intensity on the morphology of as-prepared product. The weak plasma etching makes the nanowires, while the strong plasma makes electric field on the top of nanowire much stronger, thus the etching process becomes much effective, so the cone-like shape is formed on the top of the nanowire. The medium plasma intensity just makes the morphology between cone and wire shape, as the presented nanorod here.

### 4. Summary and outlook

By using plasma etching method, aligned 1D silicon nanostructes, including nanocone, nanorod, and nanowire, have been fabricated. The plasma intensity plays an important role on the morphology of the silicon nanostructures. The nanocones can be in situ coated with thin amorphous carbon film.

The HFCVD system used in our experiments is relatively simple, cost-effective, and can be easily expanded to produce large-area high-quality silicon nanostucture arrays, which have potential application as semiconductor field emitters.

Also, a new feature in our process is the ability of producing

![Fig. 5. (a) SEM image of silicon nanowire array. (b) TEM image of a nanowire, its diameter is about 80 nm. (c) Selected area diffraction pattern. (d) EDS spectrum.](image)

![Fig. 6. Schematic model for the fabrication process of 1D silicon nanostructures with different morphologies.](image)
in situ carbon coating onto the silicon cones with a uniform coverage, which could largely enhance the field emission performance. This process avoids the complexity of post coating treatments as in conventional approaches. The coated carbon film also have the advantage of preventing surface from oxidation, and the sample possesses the equivalent merits of carbon nanotip arrays [16,17]. Therefore, the silicon nanocone arrays with in situ carbon film coating are promising candidates for applications in flat panel displays.

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