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Controlled Evolution of Silicon Nanocone Arrays Induced by Ar^{+} Sputtering at Room Temperature *

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Controlled evolution of silicon nanocone arrays induced by Ar^{+} sputtering at room temperature, using the coating carbon as a mask, is demonstrated. The investigation of scanning electron microscopy indicates that the morphology of silicon nanostructures can be controlled by adjusting the thickness of the coating carbon film. Increasing the thickness of the coating carbon film from 50–60 nm, 250–300 nm and 750–800 nm to 1500 nm, the morphologies of silicon nanostructures are transformed from smooth surface ripple, coarse surface ripple and surface ripple with densely distributed nanocones to nanocone arrays with a high density of about 1×10^{9}–2×10^{9} cm^{-2}.

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Due to the unique geometrical configurations, the higher cutoff frequency and radiation hardness, silicon nanocones have been considered to be one of the most promising materials for the antireflection surface of solar cells, the field emitter array of flat-panel displays, high-frequency devices, nanoelectronic and optoelectronic devices,[1−5] as well as the probe tip of scanning tunneling microscopy and atomic force microscopy.[6,7] As the commercial applications of field emitter arrays and the antireflection surface of solar cells, the fabrication method of silicon nanocone arrays is required to be very simple at low cost and on a large scale. In the past years, many methods have been developed to fabricate the silicon nanocone arrays, such as chemical etching,[8] reactive ion etching (RIE),[9−11] plasma etching,[12−15] the lithographical technique[16] and directly laser fabrication.[17−19] Although lithographic methods[16] have the advantage of controlling the shape, dimension and density of nanocones, the fabrication procedure is complicated and the cost of large-area fabrication is high. The other methods are very simple and suitable for large-area fabrication. However, the density of silicon nanocones is low with a range from 1×10^{6}/cm^{2} to 5×10^{8}/cm^{2} and the distribution of nanocones is not uniform. These geometrical configurations of silicon nanocones should affect the properties of field emission and antireflection. Hence, a very simple method to fabricate silicon nanocones of high density and uniform distribution should be developed for commercial applications.

One method of ion beam bombardment with metal seeded to achieve the high density of 1×10^{8}/cm^{2}–1×10^{9}/cm^{2} has been reported by Tanemura *et al.*[20] However, the distribution of silicon nanocones by this method is not uniform and the silicon nanocones appear only at the center of the crater induced by ion bombardment. In order to achieve the uniform distribution of high-density and large-area silicon nanocone arrays, the method of ion sputtering with an incident angle of 75° by using the carbon-cone-mask has been developed in our previous work[21] and the uniform and high density of 1×10^{9}–2×10^{9}/cm^{2} silicon nanocone arrays have been achieved. Therefore, this method is very simple and suitable for fabricating silicon nanocone arrays with high density and uniform distribution on a large scale and at low cost. It is believed that controlled evolution of silicon nanocones should be very important for commercial applications. In this Letter, the controlled evolution of silicon nanocone arrays induced by Ar^{+} sputtering at room temperature has been demonstrated.

A single-crystal wafer of (100)-oriented n-type silicon with the dimension of 1 cm×1 cm was used as the substrate. The experiment comprised of two steps: (i) a thin carbon film was deposited on the silicon surface by plasma enhanced chemical vapour deposition (PECVD). The base pressure was about 1×10^{-6} Torr. After the substrates were heated to and stabilized at a temperature of about 500°C, the mixture of C_2H_2 and H_2 was fed into the chamber at a flow rate 30 sccm/15 sccm (C_2H_2/H_2) and the chamber pressure was kept at 2 Torr. Plasma with a power density of 0.5 W·cm^{-2} was initiated simultaneously. A negative substrate bias of −40 V was applied to the substrate throughout the deposition process. After being deposited for 0.5 h, 2 h, 4 h and 7 h, the samples were cooled down in vacuum. (ii) Then the silicon wafers with a thin carbon coating film were sputtered by an Ar^{+} beam. The samples were brought out from the system of PECVD and then placed into the chamber of Kaufman ion source. The base pressure was about 1×10^{-5} Torr. Then the Ar gas was introduced into

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the chamber as the working gas with the pressure at 2×10^{-4} Torr. Subsequently, an Ar^+ beam with energy of 1200 eV, current density of 0.5 mA/cm^2 and incident angle with respect to the substrate surface normal of 75° was used to sputter the samples at room temperature. The sputtering time was 60 min. In order to investigate the distribution of carbon in the formation of the nanostructures, the sample after ion sputtering from 30 to 45 min were treated with boiling concentrated nitric acid solution (HNO_3) (70 wt.%) for 5 min. Then the samples were rinsed by deionized water for several times and were dried at room temperature.

The surface morphologies of samples were observed by scanning electron microscopy (SEM, LEO 1530VP). The characteristic of the carbon film was investigated by micro-Raman spectroscopy (Dilor LabRam-1B) at room temperature.

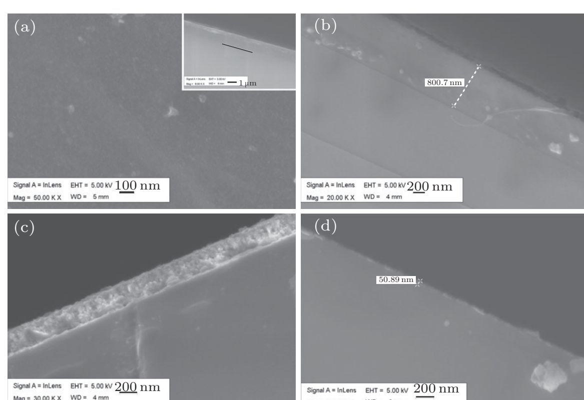

Fig. 1. (a) Surface morphology of samples with coating carbon film by PECVD for 7 h. Inset: the cross-section SEM image. (b)–(d) The cross-sectional SEM images of the samples for deposition times of 4 h, 2 h and 0.5 h, respectively.

The surface morphology and cross-sectional images of samples with the coating carbon film by PECVD for different deposited time are shown in Fig. 1. The surface of the carbon film was almost flat with random distribution of the small particles. The thickness of the carbon film with deposition times of 0.5 h, 2 h, 4 h and 7 h were about 50–60 nm, 250–300 nm, 750–800 nm and about 1.5 μm, respectively. The investigation of SEM indicates that the thickness of the carbon film was controlled by applying the different deposited time and the thickness of the carbon films from several tens nm to 1–2 μm was achieved by adjusting the deposited time from 0.5 h to 7 h in the PECVD system.

The typical SEM images of samples with different thicknesses of the coating carbon film by Ar^+ sputtering for 1 h are shown in Fig. 2 and the insert images shows the high magnification SEM images of the nanocones. With a carbon film with a thickness of about 1.5 μm, nanocone arrays with a density of about 1×10^9–2×10^9 cm^{-2} were achieved on a full area of the sample after 1 h ion sputtering and the high magnification SEM image shows that the height of the nanocone was about 300 nm and the rooter diameter was about 150 nm (Fig. 1(a)). The energy dispersive x-ray spectrum (EDX) shows that only silicon was present without carbon. When the thickness of the carbon film was 750–800 nm, the surface ripple with densely distributed nanocones was formed after 1 h ion sputtering. The height of the nanocones was about 70–80 nm, the rooter diameter was about 70–80 nm and the density of the nanocones was 0.5×10^9 cm^{-2}–1×10^9 cm^{-2} (Fig. 1(b)). With the decreasing thickness of the carbon film to 250–300 nm, the coarse surface ripple was formed and some period structures were damaged. For the sample with a thickness of 50–60 nm, the smooth surface ripple was formed. The SEM investigation indicates that with the increasing thickness of the carbon film, the surface morphology of the sample after ion sputtering experienced from smooth surface ripple, coarse surface ripple with some damaged period structure and surface ripple with densely distributed nanocones of a small size to the nanocone arrays with a density of 1×10^9–2×10^9 cm^{-2}.

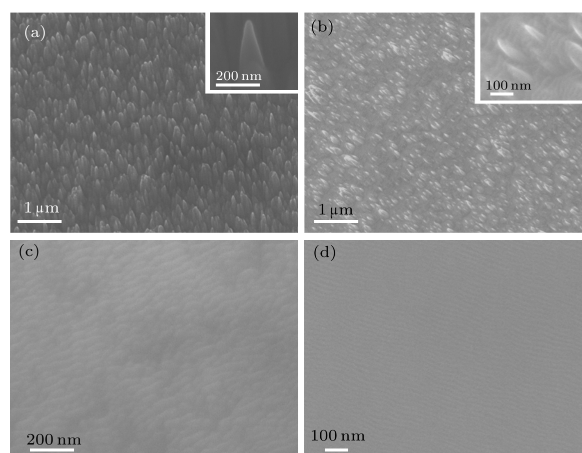

Fig. 2. Typical SEM images of samples by Ar^+ sputtering (for 1 h) for different carbon deposition times: (a) 7 h, (b) 4 h, (c) 2 h, (d) 0.5 h. Inset: the high magnification SEM images.

In order to investigate the distribution of carbon in the cone structure, the samples by ion sputtering with the initial thickness of the carbon film from 50 nm to 1.5 μm were immersed into the concentrated nitric acid solution and then the solution was heated to boiling and stabilized for 5 min. As we know, the carbon should be oxidized into carbon dioxide by boiling concentrated nitric acid solution treatment. When the carbon was removed by nitric acid solution, the morphology of silicon came out. Before and after the nitric acid solution treatment, the surface morphology was also the same, which was in accord with our previous work.[21] The result indicates that all carbon material was removed by ion sputtering, which is in agreement with the results of the EDX.

Typical micro-Raman spectra of the as-grown carbon film by PECVD for 7 h and the carbon film by ion

irradiation for 10 min and 20 min are shown in Fig. 3. There are two bands between 1000 and 2000 cm^{-1} corresponding to the typical Raman peaks of carbon materials. The peak at 1580 cm^{-1} (G band) corresponds to an E_{2g} mode of graphite, and the peak at 1330 cm^{-1} (D band) is associated with the vibration of carbon atoms with disordered graphite, such as defects, dangling bonds in plane terminations, grains boundaries, etc. The Raman spectrum is considered to depend on clustering of the sp^2 phase, bond disorder, presence of sp^2 rings or chains and the sp^2/sp^3 ratio. The intensity ratio of the D to G band models (I_D/I_G) represents the amorphous phase content or the degree of crystallinity of the carbonaceous materials.[22,23] With the increment of the ion irradiation time, the full width at half maximum (FWHM) of the D band becomes larger and I_D/I_G increases remarkably. This implies the increasing degree of the disorder and defect concentration.[22−24]

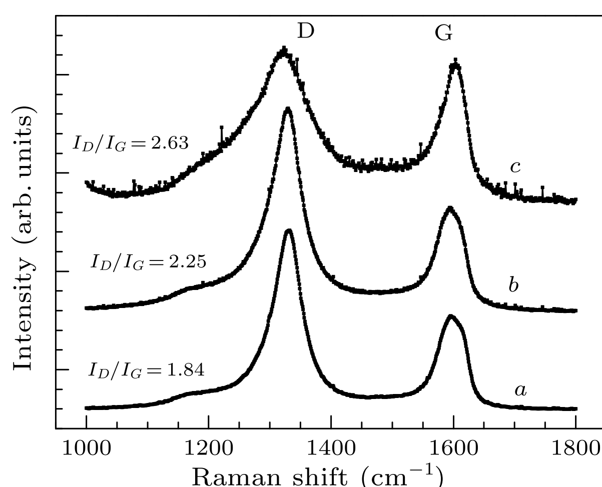

Fig. 3. Raman spectra of the coating carbon film by PECVD for 7 h (a) and the carbon film by ion sputtering for 10 min (b) and 20 min (c).

Based on the investigation of SEM, the evolution of silicon nanocone arrays could be controlled by applying a carbon film with different thicknesses as the mask. In our previous work,[21] the formation of the silicon nanocones by this method experienced a three-step process. Firstly, the Ar$^+$ sputtering with an incident angle of 75° resulted in the formation of carbon nanocones on the surface. Secondly, the carbon at the trough of cone was sputtered first, which led to the formation of cones with carbon on the top and silicon at the bottom. Finally, the carbon was sputtered completely, the morphology of carbon nanocones by Ar$^+$ sputtering was transferred onto the silicon surface and silicon nanocones were evolved. Therefore, the quality of silicon nanocone arrays was controlled by the density and size of carbon cones.

At low ion doses by oblique Ar or Xe ion sputtering graphite with the range of keV, investigated by Habenicht *et al.*,[25] the periodic ripple morphology was evolved. When increasing the ion doses, large perturbations of the surface topography occurred and even the periodic structure was damaged by the larger perturbations of surface topography.[25] When ion doses reach a critical value, the whiskers or cones could be formed on the surface, as indicated by Floro *et al.*[26] These investigations indicate that different morphologies on carbon films from surface ripple to cone arrays could be achieved by adjusting ion doses with oblique ion sputtering in the range of keV. In our previous work,[21] the evolution of surface morphology on the carbon film by Ar$^+$ sputtering has demonstrated the formation process from surface ripple to coarse cones.

In general, the ripple-like or periodic structure is formed on the solid surface by off-normal ion beam irradiation.[27] The ion-induced surface morphology is accounted for by two competitive effects, the roughening process and the smoothing process. The roughening process is caused by the different sputtering yield depending on the curvature of the surface. For a rough surface even the surface of the polished silicon wafer with the mean roughness of 0.2 nm, the sputtering yield at the trough is higher than that on the crest,[28] which should rapidly enlarge the amplitude. The smoothing process is caused by the thermal or ion-induced diffusion driven by surface energy minimization. In our experiment, the surface of the coating carbon layer was almost flat with random distribution of the small particles. Compared with the polished silicon surface, it is believed that this surface was much rougher. Also, the small particles with random distribution could be regarded as convexities on the flat surface. At the first process of off-normal ion sputtering, the smooth surface ripple could be formed due to the competitive effects of the roughening process and the smoothing process. Then, the roughening process should rapidly enlarge the roughness of the surface and convexities, enlarged convexities could transform into the protrusions and the coarse surface ripple could be evolved. With the duration of irradiation, the large perturbations could damage the periodic structure and lead to the formation of small cones on the ripple. When ion doses increased, these small cone structures on the ripple could lead to the formation of coarse cones on the whole sample surface. Hence, based on the competitive effects of the roughening effect and the smoothing effect, the surface morphology of the carbon film could be controlled by applying different ion doses. In our experiment, the carbon film acts as the mask. The thickness of the carbon film was adjusted from 50–60 nm to 1.5 µm, the time of interaction between the ion beam and the carbon film is different and ion doses increase with the thickness of the carbon film. The different ion doses should result in the different surface morphology of the carbon mask from smooth surface ripple, coarse surface ripple and densely distributed nanocones on surface ripple to cone arrays. Therefore, the morphology of the carbon mask could be controlled from smooth

ripple to cone arrays by adjusting the thickness of the carbon film.

When the carbon was sputtered, the silicon under carbon materials was exposed to the ions and then was sputtered, when all carbon materials were sputtered completely, the morphology of the carbon mask was transferred onto the silicon surface. In general, the sputter yield of silicon is only two or three times that of carbon, in the range of keV. It is believed that the amplitude of silicon nanocone arrays was only a little higher than that of carbon cones. The sputtering yield of materials under the carbon mask was several ten times that of carbon, such as Cu.[29] When carbon was sputtered, the exposed material with much higher sputtering yield would be sputtered quickly and the amplitude of morphology on the surface under the carbon mask should be enlarged at the short time. After carbon was sputtered completely, the amplitude of morphology on the surface of high sputtering yield material was much higher that of carbon mask. Ghose *et al.*[29] have reported that the fabrication of copper cone arrays with a height of several μm only required several tens nm of carbon thin film as the mask. In our experiment, the sputtering yield of silicon is only two or three times that of carbon. Therefore, the fabrication of silicon nanocones required a carbon cone as a mask. This is the reason why the silicon nanocones could be formed only in the carbon film with a thickness larger than 750 nm. In order to investigate the importance of low sputtering yield of material in this method, the films of high sputtering yield material (such as Fe and Ni) with a thickness of 2–3 μm were also used as the mask to fabricate the silicon nanostructures under the same experimental condition of ion sputtering. As a result, only smooth surface ripple on the silicon surface was formed. Due to the high sputtering yield of metal material, the amplitude of morphology on the silicon surface should decrease rapidly after the metal material was sputtered completely, hence the formation of smooth surface ripple.

The investigation of different material and different thicknesses of thin film by ion sputtering indicates that the fabrication of silicon nanocones by this method should require that the sputtering yield of material is low and the cone could be formed by ion irradiation first. The geometrical configurations will affect the antireflection and field emission properties of the silicon nanostructure. If we could control the evolution of silicon nanocone arrays, the antireflection and field emission properties should be enhanced. In the future, we will extend this work to investigate the controlled fabrication of silicon nanocone arrays (such as the density and aspect ratio) and the antireflection and field emission properties of the controlled evolution of silicon nanocone arrays.

In conclusion, we have demonstrated the controlled evolution of silicon nanocone arrays induced by Ar^+ sputtering at room temperature using the coating carbon as the mask. The investigation of scanning electron microscopy indicates that morphologies of silicon nanostructures can be controlled by applying different thicknesses of coating carbon films. Increasing the thickness of the coating carbon film from 50–60 nm, 250–300 nm and 750–800 nm to 1500 nm, the morphologies of the silicon nanostructures are transformed from smooth surface ripple, coarse surface ripple and surface ripple with densely distributed silicon nanocones to nanocone arrays with high density of about 1×10^9–$2\times10^9/\mathrm{cm}^2$. The morphology of the carbon mask with different thicknesses after ion sputtering could be controlled from the smooth ripple to the cone arrays, hence the controlled evolution of silicon nanocones. The investigation of different materials and different thicknesses of thin films by ion sputtering indicates that the fabrication of silicon nanocones by this method requires that the sputtering yield of material is low and the cone could be formed by ion irradiation at first.

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