Research Article

Fabrication of Si_3N_4 Nanocrystals and Nanowires Using PECVD

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Si_3N_4 nanowires and nanocrystals were prepared on Si substrates with or without Fe catalyst using silane (SiH_4) and nitrogen (N_2) as reactive gases through plasma-enhanced chemical vapor deposition (PECVD) technology. With Fe catalyst, Si_3N_4 nanowires were developed, indicating that Fe catalyst played a role for Si_3N_4 molecules directionally depositing into strings. The density of the nanowires is closely related to the density of Fe catalyst. When the density of Fe ions on the substrate was decreased remarkably, a smooth superlong Si_3N_4 nanowire with 12 μm in length was fabricated. Having analyzed the growth mechanism, a growth model for Si_3N_4 nanowires was developed. The growth of Si_3N_4 nanocrystallines was attributed to be a vapor-solid (V-S) deposition process.

1. Introduction

Silicon nitride (Si_3N_4) is a versatile material, which has been widely used in ceramic engines, microelectronics, nuclear power engineering, space science [1–3], and other fields due to its many excellent properties, such as high temperature resistance, high strength and modulus, and good chemical stability properties. Moreover, nanoscaled Si_3N_4 materials, quantum dots [4–6], nanotubes [7], nanowires [8, 9], and thin nanofilms [10] have superior photoelectric [11] and mechanical properties [12, 13] for the quantum confinement effects, and therefore, the improvement in device and nanocomposite performance can be predicted [14]. Various techniques, such as catalyst-assistant synthesis of a polysilazane [15], direct nitridation process [16], amorphous silicon nitride nanopowder nitridation [17], si-containing compounds carbothermal reduction-nitridation [18], chemical vapor deposition (CVD) [19], and plasma assisted chemical vapor deposition (PECVD) are used to prepare Si_3N_4 nanomaterials. Among these available techniques, PECVD has many advantages over others. A main reason is that the chemical groups in plasma has a very high energy, which can remarkably low the reaction temperature that is very useful for synthesis of both nanocrystals and nanowires. Another significant advantage is the capability of fast deposition high quality of nanocrystals and nanowires on large area substrates. Now

it has been used increasingly to synthesize various semiconductor films [20]. In this paper, using PECVD we have fabricated Si_3N_4 nanowires and nanocrystals on Si substrates with or without Fe catalyst, respectively. By decreasing the number of Fe catalyst on Si substrates to a minute, single dispersed Si_3N_4 nanowires can be obtained. Based on the analysis of scanning electronic microscopy (SEM) and X-ray diffraction (XRD), we developed a growth model for Si_3N_4 nanowires and discussed the growth mechanism as well.

2. Experiment

The studied samples were prepared on n-type Si (100) wafers by using PECVD system. Two substrates were cleaned ultrasonically with a sequence of acetone, ethanol, and deionized water, and dried by blowing N_2 . One was directly placed in the vacuum chamber; the other was coated Fe catalyst by dipping into a weak solution of FeCl_2 with some time and then put into the chamber as well. The reactive gases were silane diluted with nitrogen gas (10% SiH_4 + 90% N_2) and Ar (99.999%), with a volume ratio of 1:4. Prior to the deposition, a pretreatment of the samples in hydrogen plasma was performed at about 500°C for 10 minutes. At deposition, the substrate temperature was fixed between 400–500°C, the working pressure was kept in 40–50 Pa, and

FIGURE 1: (a) A SEM image of Si_3N_4 crystals; (b) a magnification picture.

FIGURE 2: An XRD pattern of as-synthesized Si_3N_4 nanoparticles.

the plasma power was about 50 W under an applied bias of 800 V.

In the deposition, SiH_4 , N_2 , and Ar were initially decomposed to a mixture state of Si, H, N, Ar, H_2 , and N_2 under the large bias. This mixture state is referred to as a plasma state, in which the chemical groups consisted of atoms and molecules have very high energy. A new matter of SiN was compounded feasibly at low temperatures when Si and N atoms were combined together. With SiN molecules condensed continually on the substrates, Si_3N_4 nanocrystals or nanowires were developed. The decomposition and compound processes of the experiment can be described as the following chemical reactions:

The experiment was carried out for 1 hour. The samples were removed from the chamber when they cooled to room temperature. The morphology and structure of the samples were characterized by field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD).

3. Results and Discussion

Figure 1(a) shows a surface SEM image of the sample deposited on Si substrate free of Fe catalyst at temperature of 400°C and pressure of 40 Pa. It can be seen that many cubic crystals are scattered homogeneously on the picture. The crystals take almost identical shape, that is, a normal tetrahedron structure, as clearly shown in the enlarged picture Figure 1(b). The tetrahedron structure shows that the deposited Si_3N_4 nanocrystals are characteristic of the typical diamond structure. The size of crystals also is nearly uniform, with a mean side length of $1\mu\text{m}$. The X-ray diffraction pattern of the sample is shown in Figure 2. The diffraction peaks from 19.7° , 22.0° , 26.7° , 32.9° , 33.69° , and 39.6° correspond to (101), (110), (200), (102), (201), and (301) of Si_3N_4 crystals facets, respectively. The peaks of (101) and (110) are relatively wide for some amorphous particles attached on the crystals. It confirms that the crystals are Si_3N_4 polycrystals.

For Si substrate coated with Fe catalyst by dipping in a weak FeCl_2 solution for 48 hours, Si_3N_4 nanowires were developed, as shown in the SEM images of Figure 3. Many tree-like structures made up of thin branches are distributed on the picture. We referred to the thin branches here as Si_3N_4 nanowire, on which many newly nucleated nanoparticles attached. The diameter of the nanowires is basically uniform, with a size of $0.20\mu\text{m}$; but the length is various, from 5 to $20\mu\text{m}$. Figure 3(b) is a magnification picture, where the nanowires with many Si_3N_4 nanoparticles are clearly seen. We note that one of the nanowires broke off, which might be caused by the unevenly stressing and large surface tension for it is too long.

Si_3N_4 nanowires and nanoparticles were grown on Si substrates with or without Fe catalyst under the same deposition conditions, indicating that Fe catalyst has a promote action for preferring orientationally growing, which plays a key role in the synthesis of Si_3N_4 nanowires. It has been reported that Fe ions have a directional action in the growing of nanotube and nanowires materials [21]. To explore the growth mechanism, we developed a growth model for Si_3N_4 nanowires, as shown in Figure 4. Fe ions have catalysis and play the centers of nucleation to accelerate the nucleation of Si_3N_4 that absorbed on Fe ions by Van der Waals attractive force. With a strong Van der Waals attractive force, Fe^{2+} ions can promote Si_3N_4 molecules growing in a preferred

FIGURE 3: (a) A SEM image of Si_3N_4 nanowires deposited on Fe catalyst coated Si substrate treated for 48 hours; (b) a magnification picture, the nanowires with many Si_3N_4 particles are characteristic of a tree-like structure.

FIGURE 4: A growth model of Si_3N_4 nanowires.

FIGURE 5: (a) A SEM image of single superlong Si_3N_4 nanowire growing on Fe catalyst coated Si substrate treated for 4 hours; (b) another Si_3N_4 nanowire taken in other place of the same sample.

orientation by fixing and decreasing the mobility of them. With deposition, small Si_3N_4 nanowires are formed and finally developed into long nanowires. Through branching in various directions, many nanowires with tree-like structure are finally completed on the substrate.

Many Si_3N_4 nanoparticles and amorphous are attached on the nanowires, which make the nanowires not very well. The particles are caused by too many Si_3N_4 molecules nucleated on the nanowires due to a large number of Fe ions on Si wafers. To reduce the useless particles, we decreased the concentration of Fe ions by shorting the dipping time of

Si wafer in FeCl_2 solution to 4 hours. In addition, to diminish the amorphous and to enhance the crystallization, the reactive pressure was decreased to 40 Pa and the temperature was increased to 500°C . As shown in Figure 5(a), a smooth, single, superlong Si_3N_4 nanowire without any nanoparticles is developed on the substrate. Like a tree growing from a large root, the superlong nanowire grows from a large spherical cluster. The total length is about $12\ \mu\text{m}$, and the diameter is about $0.25\ \mu\text{m}$, but becomes thinner from the bottom to the top. Moreover, the nanowire broke off at its middle, just at the mass center of the nanowire. Thus the gap may be caused by the gravity and large surface tension because the nanowire protrudes out the substrate with a slope than lies on it. Figure 5(b) is another single nanowire picture taken from other place of the sample. It grows from a cluster and ends to another one, like a long bridge between two clusters. The nanowire twisted twice showing that there is a large stress existing during growth. Obviously, by decreasing the concentration of Fe ions and the reactive pressure, the density of nanowires is significantly decreased, and the useless nanoparticles and amorphous are hardly seen on the nanowires. As a result, superlong high quality Si_3N_4 nanowires are obtained.

Since there are no liquid droplets at the tips of nanowires, which were typically observed in vapor-liquid-solid (VLS) growth mechanism [22, 23], hence in our experiment the growth mechanism of Si_3N_4 nanocrystals can be assigned to a vapor-solid (V-S) process.

4. Conclusion

A superlong single Si_3N_4 nanowire without any useless particles has been synthesized on Fe coated Si substrate using PECVD system by optimize deposition conditions including temperature and pressure. Based on the observation of SEM) we developed a model for Si_3N_4 nanowires growing, and the growth mechanism is attributed to a vapor-solid (V-S) deposition process.

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