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Formation of SiC Nanostructure Using Hexamethyldisiloxane During Plasma-Assisted Hot-Filament Chemical Vapor Deposition*

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Abstract Growth of SiC nanowires in plasma-assisted hot filament chemical-vapor-deposition by using hexamethyldisiloxane (HMDSO) as the gas source is reported. The SiC nanowires (SiC-NWs) grew on Au-coated silicon substrate with core-shell structure, where the core consisted of polycrystalline SiC grains and the shell exhibited amorphous structure. The featured structures such as cones, polyhedrons, ball-like particles were observed in the case without plasma assistance. The underlying mechanism for the growth of nanostructures was also discussed. The high chemical activity induced by the plasma process plays an important role in using monomer to generate nanostructure.

Keywords: SiC, nanowires, plasma

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1 Introduction

One dimensional (1D) nanowires have attracted considerable attention in recent years due to their ability for effective electron confinement in two dimensions as well as specific potential application in nanoelectronics[1,2]. SiC nanowires (NWs), which combine the advantages of SiC and 1D nanomaterials, are expected to exhibit more interesting mechanical, electronic and optical properties[3,4]. Great effort has been devoted to the synthesis of SiC nanowires by using different methods, such as chemical vapor deposition[5], laser ablation[6], arc discharge[7]. One strategy often used to grow nanowires is via the vapor-liquid-solid (VLS)[8,9] route. In this process, excited species from vapor are incorporated into a binary liquid alloy droplet, which acts as a transient phase leading to the material growth. As a chemical vapor deposition process is assisted with plasma application, the growing vapor becomes more complicated, and there exist lots of activated species from the dissociation of source gases. These species may be dissolved in catalyst particles, which plays an important role for the structure and composition of the formed nanometer-sized materials.

SiH₄ is often used for the growth of SiC film, where carbon in SiC comes from a separate source of hydrocarbon. It is also reported that using single molecular source compounds containing carbon and silicon elements presents good safety and enjoys low growing temperature in growing SiC[10]. Single-source precursors provide silicon-carbon-containing species in vapor via dissociation. Recently, LIN reported[11] that SiC nanocone from tetrathyl silane diluted in hydrogen by using microwave plasma CVD system.

Hot filament chemical vapor deposition (HFCVD) is one of the widely-used and convenient CVD approaches for materials growth. As a DC biasing voltage is applied to the hot filament with respect to the substrate, HFCVD is modified with plasma assistance. In this way, source gases introduced are activated and dissociated by both thermal and plasma processes.

In this work, we reported the growth of SiC nanowire in bias-assisted HFCVD by using hexamethyldisiloxane (HMDSO) as the gas source. The effect of plasma on the nanostructures obtained is investigated with/without bias application. The underlying mechanism for the growth of nanostructures is also discussed.

2 Experimental setup

The experiments were performed in a hot filament chemical vapor deposition (HFCVD) reactor with a biased substrate. The tantalum filaments were heated to a temperature around 2000°C. Source gas, HMDSO diluted with hydrogen, was introduced from the top of the chamber into the system. As passing through the hot filaments, the gas molecules were decomposed to activated species, and then diffused towards the substrate a few centimeters underneath the hot filaments. A DC electric bias was applied between the hot filaments negatively with respect to the substrate. Gold-coated silicon (100) wafers were used as substrates. As typical growth conditions, pressures of 3600 Pa was employed with a flow rate of 0.5 sccm for HMDSO and 100 sccm for hydrogen. After deposition, the samples were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), X-ray diffraction (XRD) and Raman Spectroscopy. The Raman

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measurements were carried out for visible excitation with a wavelength of 514.5 nm.

3 Results and discussion

Fig. 1 displays the SEM images and Raman spectrum of the samples in HFCVD with plasma assistance, with an applied voltage of 25 V and a substrate temperature of 450°C maintained. Fig. 1(a) and (b) refer to the samples with pretreatment, for which the gold-coated silicon (100) wafers are preheated to 800°C in a hydrogen gas environment for 20 min prior to the growth of SiC nanowires. One can find dense nanowires formed on silicon substrate surfaces, which are typically several μm long with a diameter of 40 nm to 90 nm. The nanowires exhibit various shapes, such as V-like and closed structures. The V-like nanowires, which are also called Y-junction, are considered to be arising from separation of catalyst particles [12]. The nanowires with closed structures are seldom reported, which will be characterized in detail later.

Fig.1 (a) and (b) SEM images of the sample with preheating process, (c) SEM image of the sample without preheating process, (d) Raman spectrum of the samples with preheating process

Fig. 1(c) represents the case of substrates without preheating, where only a few nanowires can be observed. By comparison, there exist much denser nanowires in Fig. 1(a) and (b), suggesting that the annealing process advances the growth of nanowires in low temperature condition.

Fig. 1(d) shows the Raman spectrum of the sample with preheating. In addition to the highest peak at 520 cm\(^{-1}\) corresponding to silicon, there exist three wide band peaks, which are centered at 610 cm\(^{-1}\), 796 cm\(^{-1}\) and 970 cm\(^{-1}\), respectively. These peaks are identified to be varieties of polytypes of SiC crystal [13]. The samples were characterized also by XRD analysis. Fig. 2 shows the XRD pattern of the sample in Fig. 1(a), and most of the reflection peaks can be indexed to 3C-SiC. Combined with the results of Raman spectrum, it is demonstrated that there exists 3C-SiC in the deposits.

As the growing temperature reached about 360°C, the initial gold catalyst layer may form gold/silicon droplets [14]. For a growing temperature of 450°C in this case, gold/silicon droplets can be induced even for samples without preheating process, and the nanowires may originate from those droplets based on the VLS route. However, the proportion of silicon to gold in the droplets for the samples without preheating would be lower than that for the samples with preheating for 20 min, because some catalyst droplets were covered simultaneously by unwanted deposits during droplet formations before the growth of nanowire, which results in nanowires of low density as shown in Fig. 1(c).

High-resolution transmission electron microscopy measurement was performed to characterize further the structure of the nanowires, as shown in Fig. 3(a). The nanowire with V-like structure is shown in Fig. 3(a), while in Fig. 3(b) one can find the polygon nanowire. Both of them have core-shell structures, with a diameter of core part less than 10 nm. Fig. 3(c) displays HRTEM image of nanowires. It is shown that the core part consists of the chain of nanocrystallites with a size varying from 2 nm to 10 nm. The mechanism for the
formation of this closed structure is not clear yet. The change in the growth direction of a nanowire may be due to stacking faults and twinning defects as well as different growth rates of amorphous sheath and crystalline core [11,15].

The TEM study and the SAED pattern, shown in Fig. 3(d), confirm that the core of nanowires consists of 3C-SiC. However, since the decomposition of HMDSO is rather complicated, it is hard to identify the composition of the amorphous shell. One fact should be noted that the molecular formula for HMDSO is \((\text{CH}_3)_3\text{Si-O-Si-(CH}_3)_3\), where the bonding strengths are 3.5 eV, 4.6 eV and 8.3 eV for C-H, Si-C and Si-O, respectively. In bias-assisted HFCVD, the average electron temperature is relatively low, typically several eV. Thus, the C-H and C-Si bonds are preferentially broken compared with that of Si-O. And those groups containing Si-O bond show a high probability to form SiO\(_x\) shell, and should be involved in the formation of SiC [16].

Without plasma assistance, we conduct the experiment at different growing temperatures. Fig. 4 shows the SEM images of the samples grown at 450°C, 550°C, and 750°C. Instead of NWs structures, various patterns have been found, such as cones, polyhedrons, and ball-like particles structure. Fig. 5 presents the Raman spectrum of the sample shown in Fig. 4(d), where one can’t find any significant Raman peak. In this case, the surface of the sample was covered by polymer-like deposits. Similar results could be obtained for other temperatures.

The one-dimensional SiC nanostructure growths can be described by the vapor-liquid-solid process. In plasma-assisted HFCVD, the dissociation of source gases is induced by both thermal activation and plasma process. There exist complicated reactions for the decomposition of HMDSO/H\(_2\) in the vapor. As a great deal of C-containing and Si-containing precursor species form in the vapor, these species move into the catalyst droplet, and react with each other to form SiC. When SiC reaches supersaturation in the liquid droplet, it will be precipitated to induce the growth of nanowires. Owing to the relatively low growing temperatures used, SiC appears in polycrystalline structures [17].

During the growth of SiC nanowire, the amorphous depositions, such as SiO\(_x\), occur on the SiC wire template simultaneously, which should be attributed to the high density of Si-O bond in the vapor and in the liquid catalyst droplet. This amorphous sheath stabilizes the nanowires and thus offers help for the growth of SiC NWs [18,19]. In addition, lots of electrons bombard on the growing surface during deposition due to the action of electric field, which leads to continuous cleaning of the catalyst surface and removal of any unwanted deposits. The bombardments of electrons on growing surface improve the chances of the incoming building units to access the catalyst particles and eventually the nucleation sites underneath.

As the plasma is turned off, the thermal activations near the hot filaments of about 2000°C are responsible for the decomposition of source gases. In this case, the plasma characteristic is very weak. Owing to lack of electron collision dissociation, HMDSO is more difficult to be decomposed into activated groups needed for the growth of SiC NWs. The deposition of polymer-like films occurs preferentially, which covers the silicon/gold droplets. The fact is that no silicon peak from the substrate is observed in Raman spectrum after turning off the plasma, as shown in Fig. 5. Under this situation, the formed polymer-like deposits impeded the active groups moving into the catalyst and therefore stopped the growth.

4 Conclusion

We used HMDSO diluted with hydrogen as the gas source to fabricate SiCNWs at 450°C in bias-assisted HFCVD. With plasma-assistance, the SiCNWs grew on gold-coated silicon substrate with core-shell structure. The core consists of polycrystalline SiC grains, and the shell exhibits amorphous characteristic. Instead of nanowires, the featured structures such as cones, polyhedrons, and ball-like particles were observed when there was only thermal activation. The high chemical activity induced by the plasma process is responsible for the observed change of growth. This study reveals
the fact that plasma process plays an important role in using monomer to generate nanostructure.

References


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