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Cubic SiC Nano-Thin Films and Nano-Wires: High Vacuum Metal-Organic Chemical Vapor Deposition, Surface Characterization, and Application Tests

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RESEARCH ARTICLE

Single-crystalline and epitaxial cubic silicon carbide (β-SiC) nano-thin films have been deposited on Si(100) substrates at a sample temperature of ~900 °C using single source precursors by the thermal metal-organic chemical vapor deposition (MOCVD) method. Diethylmethylsilane and 1,3-disilabutane, which contain Si and C atoms in the same molecule, were used as precursors without any carrier or bubbler gas. Upon increasing the deposition temperature from 900 to 950 °C, β-SiC nano-thin films with relatively small crystals and smoother surfaces were created on Si(100) substrates. Moreover, β-SiC nano-wires with 40~100 nm in diameter have also been grown selectively on nickel catalyzed Si(100) substrates with dichloromethylvinylsilane by the MOCVD method. The deposition temperature in this case was as low as 800 °C under the pressure of 5.0×10^{-2} Torr. It is worth noting that the initial growth rates of deposited β-SiC nano-thin films and nano-wires strongly depend on the deposition temperature rather than the time. In order to test the possibility of applications of these materials for electronic components such as field emitter, MEMS, and high-power transistor, we fabricated the nanoelectronic devices using both β-SiC nano-wires and nano-thin films. With these preliminary application tests, it is expected that SiC nanowires can be used as field emitter and nanoelectronic high-power transistor, and application of the SiC nano-thin films to MEMS is promising as well.

Keywords: SiC Thin Film, SiC Nanowire, MOCVD.

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1. INTRODUCTION

SiC has a wider band gap than Si and GaAs, and SiC exhibits a high electrical breakdown strength, a high thermal conductivity, a high saturated electron velocity and a good radiation resistance. Due to these properties of SiC, it is often regarded as a suitable material for high-power, high-temperature, high-frequency and high-radiation environment applications. These enable the fabrication of new classes of electronic components for applications ranging from X-, S-band and UHF transmitters to radiation-hard nuclear instruments. SiC is also physically hard and chemically inert, which is an advantage for semiconductor devices required for operating in harsh environments and micro-electro-mechanical system (MEMS) applications.[1–4] The applications of the modern SiC technologies have led to a rapid improvement in the material quality of SiC and made practical SiC devices a reality. In the meantime, the miniaturization of devices is an irresistible trend for both industrial manufacture and academic research. Nanowires are interesting building blocks for the fabrication of various devices on the nanometer scale. Therefore, the fabrication and understanding of the properties of SiC nanowires are decisive for the development of SiC-based nano-devices. Various methods have been used to grow SiC nanowires. Among them, the easiest way is the chemical vapor deposition (CVD) method. However, conventional SiC CVD process requires a high deposition temperature. Therefore, many research groups have tried to find suitable metal-organic (MO) precursors for growing SiC nano materials.[5–11]

In this work, attempts were made to grow thin films of SiC using diethylmethylsilane (DEMS) and 1,3-disilabutane (DSB) as single sources at a sample temperature of 900 °C by the CVD method on Si(100) substrates for MEMS applications. Also, we have deposited β-SiC nanowires on nickel thin film deposited over Si(100) substrates at 900 °C by the thermal MOCVD method using two kinds of single molecular precursors; dichloromethylvinylsilane (DCMVS) and DEMS.

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2. EXPERIMENTAL DETAILS

2.1. Growth of SiC Thin Films

In generally, for the heteroepitaxial growth of β-SiC on Si, the two-step (carbonization and film growth process) CVD using SiH_4 and various hydrocarbons (CH_4, C_2H_2, C_2H_4, C_3H_8 etc.) with carrier gas, is employed. This method requires an independent flow control of each source and high-growth temperature. A high-temperature process is required for the decomposition of hydrocarbon molecules, and the out-diffusion of Si from Si substrate is caused by the high-temperature process. Generally, for the crystallization of SiC, Si substrate should be held at above >1300 °C. This causes many problems at the interface of SiC and Si such as diffusion, tensile stress and lattice defects. Therefore, for the development of heteroepitaxial growth of SiC on Si, a lower substrate temperature is required (<1000 °C).

Therefore, new sources are needed, which can be used at a lower deposition temperature. The availability of single precursors that contain directly bonded Si and C atoms with a Si:C ratio of 1:1 decomposing at low temperatures may be effective for the SiC growth.

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A stainless-steel high-vacuum (HV) chamber was used for the growth of films. The reactor was pumped by turbomolecular and mechanical pump, achieving a base pressure of 2×10^{-7} Torr. Inside the reactor, the substrate was mounted on a stainless holder that was heated by a DC power supply.

The Si substrates used for the epitaxial growth in this research were cut from *p*-type (100) wafers with resistances in the range 4–10 Ω cm (rectangular shape of 28 × 8 mm^2). The substrates should be properly cleaned and prepared for the deposition in order to avoid residual surface impurities, which can create defects during growing films. Before placing them in the reaction chamber, the Si substrates were initially treated by a chemical cleaning process, which involves degreasing and acid treatment. Rinsing in deionized water and blowing-drying with nitrogen gas were used to remove contaminants on the surface.

In order to grow high quality SiC thin films, we utilized the MOCVD method. DEMS and DSB were used as single molecular precursors without carrier and bubbler gas. DSB is quite suitable as a CVD precursor for SiC due to its high vapor pressure, non-toxicity and insensitivity to air. The general deposition conditions were a working pressure of 2×10^{-6} Torr and growth temperatures in the range of 700∼1000 °C. The substrate temperature was ramped up to the growth temperature range with a constant rate while precursors were introduced. The duration of deposition ranged from 1.5–3 hr.

2.2. Growth of SiC Nano-Wires

β-SiC nanowires were grown in a home-made vertical MOCVD system. We expected that the nickel thin film plays an important role as catalyst for the growth of β-SiC nanowires, and therefore, we prepared the nickel thin film of about 20 nm in thickness on Si(100) substrate using the rf magnetron sputtering method. The Si(100) substrate was pretreated using various chemicals in an ultrasonic cleaner in the order of methanol, DI water, and acetone. DCMVS and DEMS were chosen as single molecular precursors because they have already Si—C bonds and are very volatile at low temperatures. We can suggest that these two kinds of single molecules are very suitable for growing β-SiC nanowires at low temperatures. The base pressure of the MOCVD system was 5×10^{-5} Torr, and the deposition pressure was kept at 50 mTorr. The deposition was carried out at 900 °C for 1∼3 h.

2.3. Characterization of SiC Thin Films and Nano-Wires

Several analysis and characterization techniques were employed for investigating the thin films and nanowires. Crystal structure was determined with an X-ray diffraction (XRD), and the surface morphologies were investigated by scanning electron microscopy (SEM), and atomic force microscopy (AFM). X-ray photoelectron spectroscopy (XPS) was employed to study the composition of the films. In order to further define the structure of the β-SiC nanowires, transmission electron microscope (TEM) images and transmission diffraction (TED) patterns were obtained. To identify the composition of the β-SiC nanowires, not only XPS but also energy dispersive X-ray (EDX) analysis were carried out.

3. RESULTS AND DISCUSSION

The XRD technique was employed to verify the phase and the orientation of deposited β-SiC films as well as to their lattice parameter. Figure 1 shows a θ–2θ XRD scan for

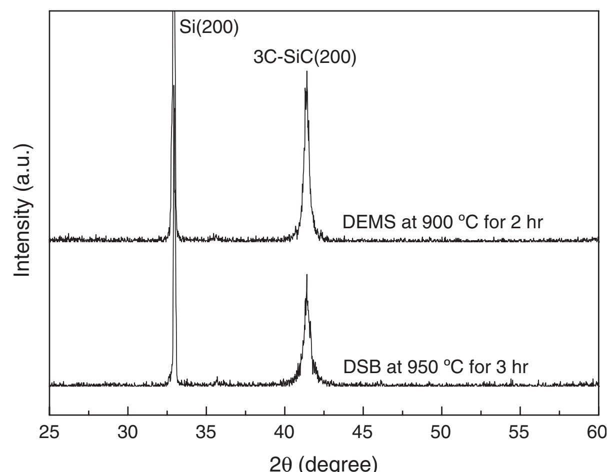

Fig. 1. XRD patterns of β-SiC thin films grown on Si(100) using DEMS and DSB precursors.

β-SiC films deposited on Si(100) substrate using DEMS at 900 °C for 2 hr and DSB at 950 °C for 3 hr. As shown in Figure 1, intense reflection peaks of β-SiC(200) was observed at $2\theta = 41.4°$, indicating that the deposited β-SiC film has a single phase cubic structure.

X-ray photoelectron survey spectrum obtained from the as-grown β-SiC films deposited at 900 °C for 2 hr. The survey spectrum clearly shows the photoelectron peaks of Si 2s, Si 2p, C 1s, and C (KLL) Auger signals, indicating the formation of the SiC film (not shown). There also appear O 1s and O (KLL) Auger peaks, which can be attributed to surface contaminations by air and/or moisture during sample transfer. The Si:C stoichiometry of this film is estimated to be 1:1.2.

SEM images of β-SiC thin films created using DEMS at 900 °C are displayed in Figure 2(a). In the low temperature range, SiC films are thin and have smooth surface morphologies and consist of nano-size crystals (not shown). With increasing the deposition temperature to 900 °C or 950 °C, relatively larger crystals can be seen (Fig. 2(a)). This result implies that at deposition temperatures over 800 °C, crystal sizes and crystallinity of SiC thin films are dependent on substrate temperature. The shape of the crystal synthesized at 900 °C is mainly square-like and the best quality of a SiC film can be obtained between 900 and 950 °C. However, the film has a relatively rough surface morphology compared to the films grown below 800 °C. Figure 2(b) shows SEM images of β-SiC thin films grown using DSB at 950 °C. SiC thin films grown over 900 °C are thick (for example, 1 μm for 950 °C) and have rough surfaces. This means that SiC thin film using DSB is not suitable for MEMS applications despite the good growth rate because of its rough surface. We firstly deposit SiC thin films at a low temperature for obtaining smoother surfaces, and then a high temperature was used for further deposition. From these two steps processes, we could obtain very smooth films. It is expected that SiC cantilevers have much higher resonant frequencies than conventional cantilevers and that application of SiC thin films to MEMS should be promising.[12]

From the AFM images, more detail information on film morphology can be gained. Figures 2(c), (d) shows the AFM images of β-SiC films on Si(100) grown using DEMS at 900 °C and using DSB at 950 °C. The root-mean-squares (RMS) roughnesses of grown films of Figures 2(c) and (d) are approximately 32 nm and 12 nm, respectively.

Figure 3 shows the XRD patterns of the β-SiC nanowires deposited on nickel covered Si(100) substrates under 50 mTorr, and 900 °C for 3 hr. using (a) DCMVS and (b) DEMS. They show the crystalline peaks at $2\theta = 35.6°$, 41.4° and 60.0°, which are attributed to the β-SiC(111), (200) and (220) planes, respectively. Peaks from either the other phases of SiC or the nickel catalyst are absent. The SiC nanowires grown by two different precursors show the same diffraction pattern and tendency. Conclusively, XRD analysis shows that the deposited β-SiC nanowire on nickel-deposited Si(100) substrate has a polycrystalline zinc-blende structure at 900 °C. The β-SiC nanowire grown by DCMVS shows a better crystallinity than that of the SiC nanowire deposited by DEMS.

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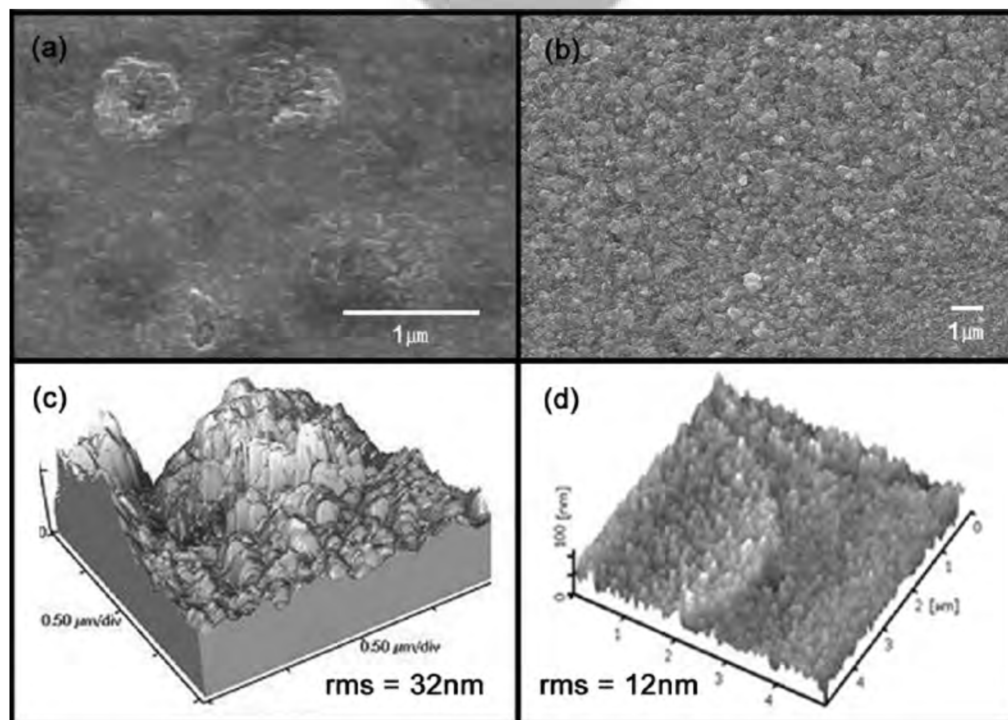

Fig. 2. SEM and AFM images of the β-SiC films deposited on Si(100) substrate (a), (c) using DEMS at 900 °C (b), (d) using DSB at 950 °C.

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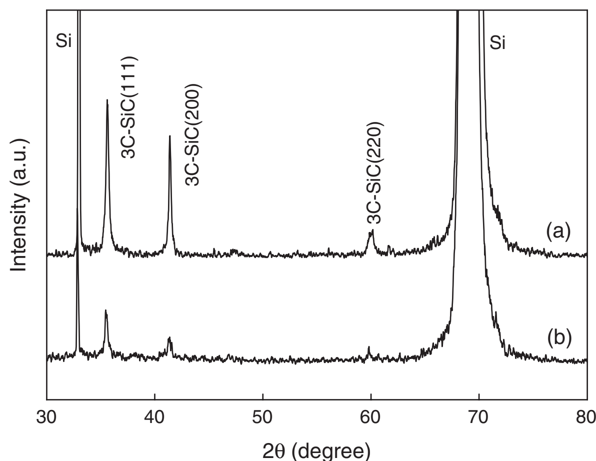

Fig. 3. XRD patterns of the β-SiC nanowires deposited on nickel-deposited Si(100) substrates under 50 mTorr, and 900 °C for 3 hr using (a) DCMVS and (b) DEMS.

Figure 4 shows the typical SEM images of the obtained β-SiC nanowires grown by (a) DCMVS and (b) DEMS at 900 °C. It can be clearly seen that straight nanowires are randomly grown on the substrate with a high density. The differences of two SEM images are the thickness and length of grown SiC nanowires. In the case of DCMVS as precursor (Fig. 4(a)), nanowires of about 40~100 nm in diameter and over 10 μm in length can be easily grown. However, in the case of DEMS (Fig. 4(b)), deposited SiC nanowires are thicker and shorter, and the surface roughness is much higher than that of Figure 4(a).

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To investigate more detailed structure of as-deposited β-SiC nanowire, TEM studies combined with EDX analyses were performed. For TEM experiments, the β-SiC nanowires grown at 900 °C were prepared. Figure 5 shows a typical TEM image obtained from a single β-SiC nanowire. TEM shows existence of the β-SiC nanowires with a diameter of about 100 nm, which are wrapped by an amorphous layer with a thickness of about 2 nm. We can confirm by EDX data that this layer is amorphous carbon. Because the metal-organic sources used in this experiment have high carbon contents, we could guess that this amorphous carbon layer should be originated from the precursors. Also, TEM image of this nanowire shows that they

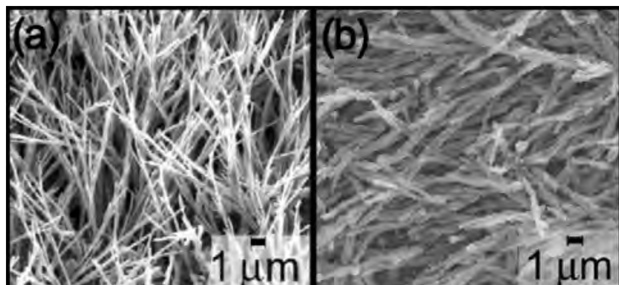

Fig. 4. Typical SEM images of the obtained β-SiC nanowires grown by (a) DCMVS and (b) DEMS at 900 °C.

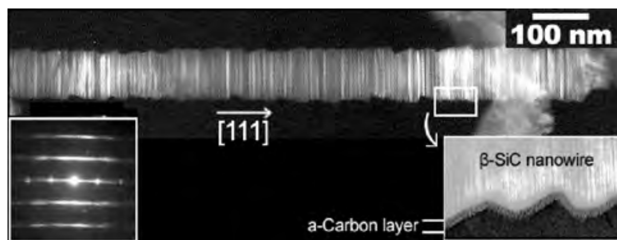

Fig. 5. Typical TEM image of a single β-SiC nanowire grown at 900 °C. Inset (left) shows the electron diffraction pattern of the same sample, and insert (right) shows a zoom-image of β-SiC nanowire.

are crystalline with defects, including numerous stacking faults, etc. We speculate that the nanowire was grown via the vapor–liquid–solid (VLS) process from a nickel-containing catalytic droplet, although the catalytic droplet was not observed at the end of the nanowire because the nanowire was broken and the droplet was removed during the ultrasonic treatment. Based on this speculation, we can thus guess that changes in diameter and well-defined facets can be recognized from the β-SiC nanowire grown via the VLS process from catalytic droplet. These two features indicate that stick-slip motion occurred during the growth; when sticking, the diameter, which was defined by the area of the LS interface, increased to form energetically favorable facets. When growing along the facets, the diameter became larger, then the wetting angle became smaller and the component of VL interface tension in the LS interface became larger. Eventually the droplet slipped driven by LS and VL interface tensions resulting in an abrupt decrease in diameter.[13] The inset image (left) of Figure 5 shows the electron diffraction (ED) pattern of a selected area obtained from the same sample. It shows the bright spots corresponding to β-SiC(200) and (111), and streaks, which are perpendicular to the stacking faults. These stacking faults are generally thought to be originated from thermal stress during the growth process.[11] EDX spectrum corresponding to the stem of a β-SiC nanowire was also investigated. There are only three peaks assigned to Si, C, and Ni. Based on quantitative analyses of the stem of a β-SiC nanowire, the average atomic ratio of Si and C is estimated to be about 1.0:1.2, whereas that of surface regime wrapped with carbon about 1.0:11.5, respectively.

For electrical transport measurement, the as-grown SiC nanowires were prepared on Si wafer pre-patterned by a standard photolithography process. The length and diameter of a measured SiC nanowire were about 10 μm and 100 nm, respectively. A linear I–V curve and thus suggests that the electrical contacts for the device with electrodes are almost ohmic (not shown).[14] It indicates that the resistance between electrodes and nanowire, which was surrounded with carbon layers, is not higher than that of nanowires wrapped by oxide layers. From I–V characteristics of the β-SiC single nanowire, the resistance value, calculated by the slope of the graph, is approximately 2×10^5 Ω. We can suggest that electrons can be more

easily transferred through the surface of the SiC nanowires than that of stem of the SiC nanowires. The dependence of the stem (gate) of the SiC nanowre without the thinner carbon layer is currently studied.

4. CONCLUSION

We have deposited the SiC thin films on Si(100) substrate by DEMS and DSB as single precursors at temperature range of 700∼1000 °C. At these deposition conditions, the major crystal form is β-SiC and the values of RMS and roughness are approximately 32 nm and 12 nm, respectively. These results show that the deposition temperature and time could be one of the important factors for influencing the film crystallinity. The XPS result shows that the SiC film grown at 900 °C is slightly carbon-rich. Application of SiC thin film, which is famous for its superior intrinsic properties, will be readily adaptable to MEMS applications.

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Cubic silicon carbide (β-SiC) nanowires have been deposited on nickel thin film over Si(100) using a single molecular precursor at 900 °C by the MOCVD method. DCMVS and DEMS were used as single precursors without any carrier and bubbler gas to increase mass transportation or to remove contaminants in the nanowires.

XRD and SEM analyses show that the deposited β-SiC nanowire on nickel-deposited Si(100) substrate has a polycrystalline zinc-blende structure at 900 °C, and the β-SiC nanowires from DCMVS as a precursor have a good crystallinity with smoother surfaces than that from DEMS. High-resolution TEM analysis showed a detailed structure that amorphous carbon layers surround the as-deposited β-SiC nanowires, and the β-SiC nanowire has [111] growth direction with a well-crystallized structure. Based on the XPS and EDX analyses, the atomic composition ratio of Si to C was obtained to be 1:1.2, indicating existence of carbon-rich species on surface regions. I–V data shows an ohmic contact behavior due to these carbon-rich layers located in the surface regime with an atomic composition ratio of Si to C of 1.0:11.5, suggesting possible applications to both electronic devices and field emitter.

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