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Growth and Chemical Thermodynamics Analysis of SiC Film on Si Substrate by Heating Polystyrene/Silica Bilayer Method

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SiC films were prepared by modified heating polystyrene/silica bilayer method on Si (111) substrate in normal pressure flowing Ar ambient at 1300 °C. The films were investigated by Fourier transform infrared absorption, X-ray diffraction, and scanning electron microscopy measurements. The chemical thermodynamics process is discussed. The whole reaction can be separated into four steps. The carburizing of SiO is the key step of whole reaction. The main reaction-sequence is figured out based on Gibbs free energy and equilibrium constant. Flowing Ar is necessary to continue the progress of whole reaction by means of carrying out accumulating gaseous resultants. The film is very useful for application in a variety of MOS-based devices for its silica/SiC/Si(111) structure, in which the silica layer can be removed thoroughly by the standard RCA cleaning process.

Key words: Thin films, Heat treatment, Silicon carbide, Chemical thermodynamics, Silicon monoxide

I. INTRODUCTION

Due to its excellent properties including wide band gap, high electric breakdown field, high thermal conductivity, high carrier saturation velocity and good chemical stability, silicon carbide (SiC) has become a key material of the third-generation semiconductor [1], which can be used under extreme conditions such as high-temperature, high power and high frequency [2,3]. Moreover, SiC has a unique attribute compared with other compound semiconductors: it can be thermally oxidized to produce silica layer. This makes it possible to fabricate a variety of MOS-based devices [4].

However, the high expense of bulk crystal and size limitation of SiC wafers have seriously restricted its applications. Therefore, heteroepitaxial growth of high quality SiC film has become very attractive [5]. In heteroepitaxial growth of SiC film, Si is most frequently selected to be the substrate profiting from its high quality, large wafer and low cost. Moreover, taking advantage of a limited leakage current, the SiC/Si heterojunction is used in bipolar transistors, solar cells, photodiodes and phototransistors. In heteroepitaxial growth of SiC film on Si substrate, techniques such as chemical vapor deposition (CVD) [6], pulsed laser deposition (PLD) [7] and molecular beam epitaxy (MBE) [8] have been frequently used. However, one of the problems associated with heteroepitaxial growth of SiC on Si is the formation of cavities at the SiC/Si interface. It is important to eliminate the cavities to enhance the performance of the devices.

Several techniques have been adopted to suppress the cavity formation. Sun *et al.* found that cavity-free SiC film could be obtained by growing $a > 10$ nm SiC buffer layer before the CVD growth [9]. Friessnegg *et al.* reported that combining low temperature deposition with high temperature annealing could also be an effective approach to avoid cavities [10]. However, our recent results [7,11] based on pulsed laser deposition (PLD) technique revealed that the cavities still exist after annealing. In these cases, the cavities may result from the Si deficiency forming in the growth process. It was reported that the loss of Si atoms at the SiC surface is compensated by the migration of Si atoms from the substrate [12].

In our previous work [13], we reported the method of growth of crystalline SiC film free of cavities by heating polystyrene/silica (PS/silica) sol-gel coating on Si(111) substrate in vacuum (10^{-3} Pa). However, this method has the disadvantage that the thickness of the silica layer is hard to control. The fabricated sample is sometimes SiC/silica/Si(111) structure. To overcome this disadvantage, the growth process is modified in the present work. A gaseous reaction is used to grow SiC film on upper Si(111) substrate, under which the PS/silica/Si(111) nappé is placed as reaction source.

The film fabricated by this modified method was silica/SiC/Si(111) structure which is useful for application of silicon carbide semiconductor-devices. In addition, the silica layer on the film can be removed absolutely by the RCA cleaning process. Scanning electron microscopy (SEM) measurement of the film cleaned by RCA cleaning process reveals a smooth surface. No cavities, which are frequently observed in SiC/Si heterostructure grown using many other techniques [14-18], were formed at the interface. The mechanisms of the reaction process were discussed on the analysis of

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chemical thermodynamics.

II. EXPERIMENTS

The process of preparing PS/silica sol-gel bilayer on Si substrate was described in detail in a previous work [13]. Si(111) wafers with the resistivity of 8-13 $\Omega\cdot\text{cm}$ were used as the substrate after RCA cleaning. A tetraethylorthosilicate (TEOS)-derived OCS (organic compound of silicon) sol-gel layer was deposited by spin coating at 3500 r/min on the substrate. After the aging and drying processes, the silica/Si sample was prepared. PS grain was dissolved into toluene to produce solution. Then a PS layer was spin-coated on the silica layer at 3000 r/min to form PS/silica/Si(111) structure. After the aging and drying processes, the PS/silica/Si sample was placed on the bottom of a graphite crucible as source substrate. A Si substrate was cleaned by RCA process and placed upon the source substrate with the polished surface facing the source substrate (but not in direct contact). The graphite crucible was placed in a quartz tubular furnace and heated in static ambient Ar at 1200 $^{\circ}\text{C}$ for 20 min keeping the pressure at 10^5 Pa, and then heated in normal pressure flowing ambient Ar at 1300 $^{\circ}\text{C}$ for 30 min. The growth chamber had been pumped and washed by Ar before heating.

For comparison, PS layer was spin-coated directly on the Si(111) substrate which was cleaned by RCA cleaning process (denoted as PS/Si), and then heated under the same conditions as source substrate.

The composition and surface morphology of the films were investigated by Fourier transform infrared absorption (FTIR, MAGNA-750), X-ray diffraction (XRD, P/Max-RA, Cu $K\alpha$), and scanning electron microscopy (SEM, X-650) measurements. In FTIR spectra, the information of the silicon substrates was subtracted for comparison.

III. RESULTS AND DISCUSSION

A. Analysis of upper film

The FTIR spectra of upper films corresponding to source substrate PS/silica/Si and PS/Si respectively are plotted in Fig.1. Two absorption bands, that is, vibration of Si-C stretching mode at $\sim 800\text{ cm}^{-1}$ and Si-O stretching mode at $\sim 1070\text{ cm}^{-1}$ are observed in curve (a). However, the 1070 cm^{-1} absorption band is absent in curve (b).

The upper film correspond to source substrate PS/silica/Si was then cleaned by RCA process. FTIR spectra of the as-deposited and as-cleaned film are plotted in Fig.2. From FTIR spectra, it can be seen that the SiO_2 layer on upper film disappeared absolutely after RCA cleaning process. This suggests that the SiO_2

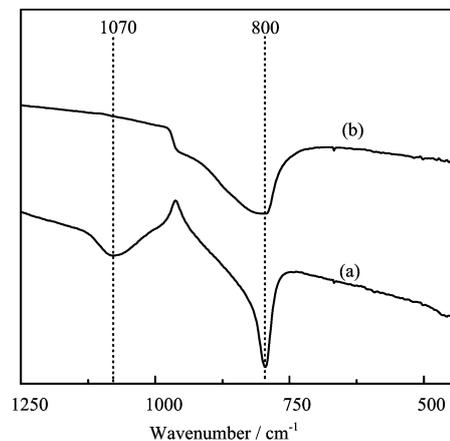


FIG. 1 FTIR spectra of upper films corresponding to source substrate (a) PS/silica/Si and (b) PS/Si.

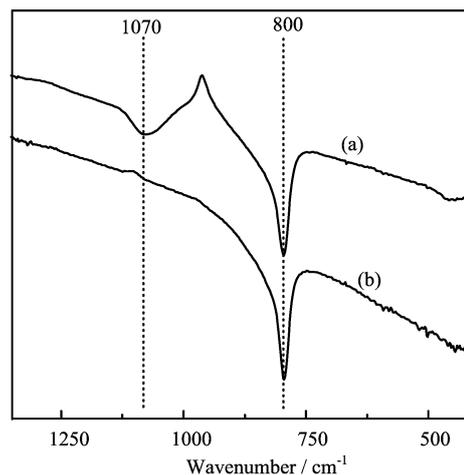


FIG. 2 FTIR spectra of as-deposited (a) and as-cleaned (b) upper films.

layer just formed at the cooling down process right after the formation of the SiC layer.

The surface morphology of the as-cleaned film was investigated by SEM measurements, as illustrated in Fig.3. One can see that the film surface is very smooth and free of triangular defects.

Figure 4 shows the XRD pattern of the as-cleaned film. One can see from the pattern that the peak at $2\theta=35.6^{\circ}$ corresponds to the 2.51 \AA spacing of close packed planes of silicon carbide. Intensities of other SiC peaks are very weak, which suggests that the as-cleaned film displayed a preferential orientation toward the close packed direction.

Above all, the data suggest that the reaction process of this system in the case of PS/silica/Si source substrate may be the following: (i) PS pyrolyzed at 400 $^{\circ}\text{C}$ and formed fragments of hydrocarbon. Majorities of hydrocarbon fragments were absorbed by the silica layer which had a rough and large area surface and minorities of hydrocarbon fragments were absorbed by upper

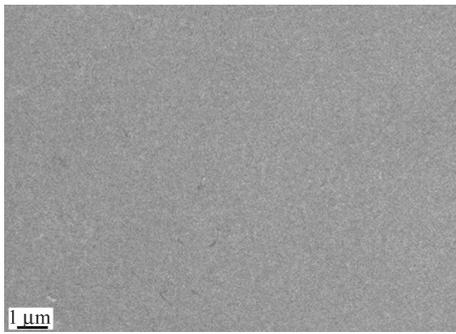


FIG. 3 SEM image of the as-cleaned upper film.

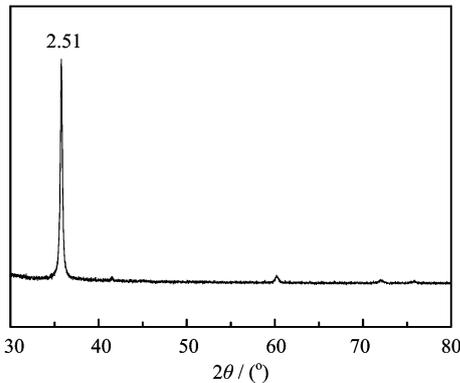
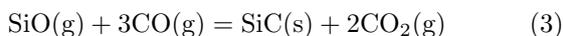
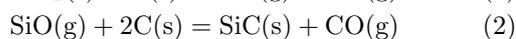
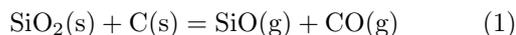


FIG. 4 XRD pattern of the as-cleaned upper film.

Si substrate. (ii) At 1200 °C, the C atoms that arose from the pyrolysis of hydrocarbon fragments reacted with the upper Si substrate and formed a thin silicon carbide buffer layer. (iii) At 1300 °C, the C atoms that arose from the pyrogenation of hydrocarbon fragments reacted with the silica layer and formed gaseous SiO. Then a carburizing reaction of gaseous SiO occurred subsequently. (iv) During the cooling down process, residual SiO deposited on the as-grown film and at last transformed into SiO₂. In the PS/Si case, gaseous SiO cannot form without a silica layer on the source substrate, leading to the absence of the absorption band at 1070 cm⁻¹, as shown in Fig.1 curve (b).

B. Chemical thermodynamics analysis of reaction process

Main reactions of SiC formation process:



It can be seen that almost all of the gaseous SiO in our system is supplied by reaction (1). According to basic

formula of chemical thermodynamics:

$$\Delta H = \Delta H^o + \int_{298}^T \Delta C_p dT \quad (4)$$

$$\Delta S = \Delta S^o + \int_{298}^T \frac{\Delta C_p}{T} dT \quad (5)$$

$$\Delta G = \Delta H - \Delta S \quad (6)$$

$$= \Delta H^o + \int_{298}^T \Delta C_p dT - T\Delta S^o - T \int_{298}^T \frac{\Delta C_p}{T} dT$$

$$K_p = \exp\left(\frac{-\Delta G}{RT}\right) \quad (7)$$

The equilibrium constant of reaction (1) at 1300 °C can be calculated as:

$$K_{p1} = \frac{p_{\text{CO}} p_{\text{SiO}}}{p^0} = 5.58 \times 10^{-4} \quad (8)$$

where P^0 is standard pressure.

SiC was formed through competitive carburizing reactions of gaseous SiO involved in reaction (2) and reaction (3).

As majorities of hydrocarbon fragments were absorbed by the silica layer, reaction (2), which is a gas-solid reaction, almost occurred at source substrate. Reaction (3), which is a gas-gas reaction, would occur at both source and upper substrates. In our system, reaction (3) is a key reaction for SiC growth on the upper substrate.

Based on ΔG , at the same temperature, reaction (2) is the preferential reaction because it has a smaller ΔG than reaction (3). The equilibrium constant of reaction (2) at 1300 °C constant temperature process can be calculated as:

$$K_{p2} = \frac{p_{\text{CO}}/p^0}{p_{\text{SiO}}/p^0} = 141.8 \quad (9)$$

In equilibrium phase, the equilibrium partial pressure of SiO should have a direct-proportion relationship with the equilibrium partial pressure of CO. However, in our system, required SiO was only supplied by reaction (1) and equilibrium partial pressure of SiO and CO are restricted by the equilibrium constant of reaction (1). The equilibrium partial pressure of SiO has an inversely-proportional relationship with the equilibrium partial pressure of CO.

From simultaneous Eqs. (8) and (9), it can be calculated that: when the partial pressure of CO reaches 28 kPa, reaction (1) has an equilibrium with reaction (2), and the equilibrium partial pressure of SiO supplied by reaction (1) is 200 Pa which equals the required equilibrium partial pressure of SiO for reaction (2). After this, if reaction (2) continues its process, with the

progress of reaction (2), the pressure of CO will keep on rising and reaction (1) will be restrained by excess pressure of CO, and the SiO supplied by reaction (1) will not meet the requirements of reaction (2). As a result of lack of gaseous SiO, reaction (2) will be restrained. Hence, if pressure of CO reaches 2.8×10^4 Pa, reaction (2) will not be the most preferential reaction. In such conditions, reaction (3) would be more preferential because CO and SiO are both the reactants of reaction (3) hence the high pressure of CO would boost reaction (3) and simultaneous consumption of SiO and CO would also boost the process of reaction (1). In this case, SiO would keep on being supplied. SiC could grow on upper substrate.

However, with the progress of reaction (3), the pressure CO_2 would keep on rising, accumulating CO_2 would restrain the process of reaction (3) and accumulating CO_2 would transform into CO in the graphite crucible, so that pressure of CO in the system would keep on rising.

Thus, in a static ambient Ar reaction system, accumulated CO would restrain reaction (1) at anaphase. The lack of SiO results in interruption of reaction (2) and (3). Figure 5 is the FTIR spectra of upper films corresponding to different treating times (30, 60, and 90 min) in static ambient Ar reaction system. Compared with the FTIR spectrum of the upper film which is treated in flowing Ar ambient, as illustrated in Fig.1(a), the intensities of the absorption bands at 800 cm^{-1} of all samples are much weaker and seem independent of the treating time. This result is consistent with our thermodynamic analysis.

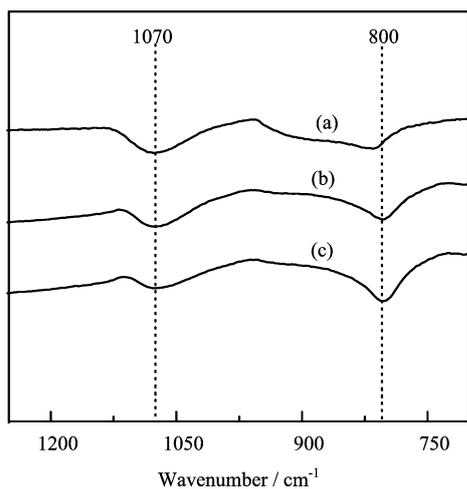


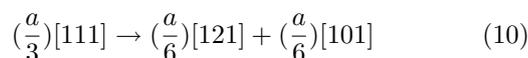
FIG. 5 FTIR spectra of upper films corresponded to different treating time (a) 30 min, (b) 60 min, and (c) 90 min in static ambient Ar reaction system.

In the system with flowing ambient Ar, flowing Ar would carry out accumulating CO and CO_2 from the graphite crucible, leading to the decrease of partial pressure of CO and CO_2 . Hence the whole process would continue.

In the cooling down process, residual SiO deposited on the substrate and formed into SiO_2 with CO at last through the counter reaction of reaction (1) which had a positive ΔG and ΔS .

C. Mechanism of suppression of interfacial cavity

It is generally accepted [19-21] that the cavities originate from out-diffusion of substrate Si atoms which starts at inhomogeneous regions on the substrate surface. The out-diffusion leads to the formation of Si vacancies. At high temperature, the evaporation rate of Si atoms is expected to be quite large (e.g. 10 monolayers per second at $1300 \text{ }^\circ\text{C}$ in vacuum [22]). The Si vacancies are inclined to coalesce in a close-packed (111) plane due to its lowest surface energy, forming an intrinsic stacking fault with three boundaries parallel to $\langle 110 \rangle$ directions, which is closed by three Frank sessile dislocations. The sessile dislocation may decompose to form two imperfect dislocations to lower the total energy according to



The imperfect dislocations $\left(\frac{a}{6}\right)[121]$ then diffuse to three adjacent $\{111\}$ planes by the repulsion of $\left(\frac{a}{6}\right)[101]$, leaving new stacking faults between them. These stacking faults in the four $\{111\}$ planes are bounded to produce an upside-down tetrahedron. The tetrahedron appears as a triangle when the substrate surface is oriented toward $\{111\}$ planes, while appearing a quadrangle when the substrate surface is $\{100\}$ planes [24]. Many observations [12,24-26] on cavity shape have confirmed this prediction. Hence it is clear that the cavity is in fact formed by stacking faults in the substrate. Moreover, due to the relatively low formation energy of stacking fault [26] in silicon carbide materials, the cavity can elongate into the film, and even reach the film surface.

When SiC films are grown by vapor methods such as CVD, it was reported [9] that the Si substrate serves as a reservoir of Si source for SiC formation at the initial stage of growth. This is one of the driving forces of Si out-diffusion.

According to the above discussion, it is easy to understand the essential points of suppressing the formation of the cavities including control of Si out-diffusion and Si source supply for SiC formation.

In the present work, we use standard atmosphere Ar ambient, thus the evaporation rate of Si atoms is much smaller than that in vacuum ambient. It is reported [22] that the evaporation rate of SiC is very small and the diffusion coefficient of Si in SiC is negligible. When an island of SiC is formed, Si out-diffusion at that point would be effectively suppressed. When a continuous large area of SiC is formed, the Si out-diffusion would

stop. Hence in the present work, after the thin silicon carbide buffer layer was formed at 1200 °C, Si out-diffusion was suppressed successfully. At 1300 °C, the silica layer (SiO₂) reacted with C atoms from the pyrolysis of hydrocarbon fragments and formed SiO, thus the supply of Si source was ensured. Therefore, the formation of cavities is suppressed effectively in our experiment.

IV. CONCLUSION

SiC films were prepared by modified heating PS/Silica bilayer method on Si (111) substrate in flowing ambient Ar at 1300 °C. The film fabricated by this modified method was silica/SiC/Si (111) structure, in which the silica layer can be removed absolutely by RCA cleaning process. The XRD pattern of the as-cleaned film shows that the film displayed a preferential orientation toward the close packed direction.

The whole reaction can be separated to four steps. The carburizing of SiO is a key step. At first, reaction (2), which has a smaller ΔG than reaction (3), is the preferential reaction. When pressure of CO reaches 2.8×10^4 Pa, reaction (2) is restrained, and reaction (3) is more preferential. Pressure of CO of the whole system keep on rising with progress of the whole reaction, therefore flowing Ar ambient, which is introduced to accelerate the flow of ambient and carry out cumulate gaseous resultants, is necessary.

Plan-view SEM of the SiC film after the RCA cleaning process shows a very smooth surface with no triangular defects. In the present work, we used standard atmosphere Ar ambient and a thin silicon carbide layer to suppress the out-diffusion of Si atoms. A silica layer on the source substrate is used to ensure the supply of Si source.

V. ACKNOWLEDGMENT

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