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Growth Kinetics of Silicon Carbide Film Prepared by Heating Polystyrene/Si(111)

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SiC films were prepared by heating polystyrene/Si(111) in normal pressure argon atmosphere at different temperatures. The films were investigated by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and Fourier transform infrared absorption measurements. The thicknesses of SiC films were calculated from FTIR spectra. The growth kinetics of the growth process of SiC films were investigated as well. The thicknesses of the SiC films grown for 1 h with increasing growth temperatures have different trends in the three temperature ranges: increasing slowly (1200-1250 °C), increasing quickly (1250-1270 °C), and decreasing (1270-1300 °C). The apparent activation energies of the growth process of SiC films in the three ranges were calculated to be 122.5, 522.5, and −127.5 J/mol respectively. Mechanisms of the different growth processes were discussed. The relation between film thicknesses and growth temperatures indicated that the growth process was a 2D mechanism in the first range and 3D mechanism in the second range. In the third range, the thicknesses of SiC films were decreased by the volatility of Si and C atoms.

Key words: Thin films, Silicon carbide, Fourier transform infrared absorption, Growth kinetics

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, this unique combination of properties makes this material suitable for very high speed microprocessors. In particular, cubic SiC (3C-SiC), which has zincblende structure, exhibits a band gap (E_g≈2.3 eV at 300 K) and quite good electrical properties, such as high electron mobility and saturation drift velocity in comparison with the other polytypes [4,5]. Furthermore, SiC has a unique attribute compared with other compound semiconductors. It can be thermally oxidized to produce a silica layer. This makes it possible to fabricate a variety of MOS-based devices [6].

However, the high expense of bulk crystal and size limitation of SiC wafers have seriously restricted the development of SiC devices. Therefore, heteroepitaxial growth of high quality SiC film has become very attractive [7-9]. In heteroepitaxial growth of SiC film, Si is most frequently selected to be the substrate due to 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) [10-12], pulsed laser deposition (PLD) [13-15], and molecular beam epitaxy (MBE) [16-18] have been used frequently.

To grow high-quality SiC film on Si substrate, it is necessary to comprehend the growth kinetics of SiC film. Because the film is thin and located on Si substrate, some common techniques are inadequate to detect the film. In this situation, Fourier transform infrared absorption (FTIR) is useful to detect the film. The infrared lattice absorption band can give some information about the film, such as the vibration of the Si−C bond. Mogab introduced a formalism to determine the thickness of SiC film from the infrared spectrometry [19]. The growth rates $K(T)$ of SiC films can be calculated according to the relative thicknesses of SiC films versus growth temperatures. The growth rates of SiC films can also be expressed as a function of growth temperatures T by the Arrhenius expression. Then the apparent activation energies of the growth process of SiC films in the different ranges can be calculated.

In this work, SiC films which are useful for application

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of silicon carbide semiconductor-devices were grown on Si(111) by reaction between Si substrates and hydrocarbons produced from pyrogenation of polystyrene (PS). We had qualitatively and quantitatively analyzed the FTIR spectra of the SiC films grown at different temperatures. The thicknesses of SiC films were calculated from the lattice absorption bands [19]. The apparent activation energies of the growth process of SiC films in different ranges were calculated. Some explanations are proposed for the mechanisms of the different growth process of SiC films.

II. EXPERIMENTS

Si(111) wafers with the resistivity of 8-13 Ω·cm and a size of 10 mm×10 mm used as substrates were cleaned by the RCA (Radio Corporation of America) process. PS were dissolved into toluene in constant temperature (40 °C) water bath heating for 24 h to prepare PS sol. Then PS sol-gel layers were deposited by spin coating at 3500 r/min on Si substrates to form PS/Si(111) structure. After an aging and drying process at 60 °C in air for 24 h, the PS/Si(111) sample was placed on the bottom of a semi-airtight quartz crucible. The quartz crucible was placed in a quartz tubular furnace and heated in static ambient Ar at 400 °C for 1 h. Small hydrocarbon molecules arose from pyrogenation of PS at 400 °C, and then the quartz crucible was heated in ambient Ar at different growth temperatures for 1 h in turn. During heating, the pressure of Ar was kept at 101 kPa. The growth chamber had been pumped and washed by Ar before heating. The temperature error of the quartz tubular furnace is ±0.5 °C, which is far less than the temperature interval of our experiment. The temperature error can meet the requirement of precise temperature control.

The composition, structure, and surface morphology of the films were investigated by X-ray diffraction (XRD, P/Max-RA, Cu Kα), X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Mg Kα), and scanning electron microscopy (SEM, Hitachi X-650). The FTIR measurements were carried out all along 400-4000 cm^{-1} on a MAGNA-IR 750 spectrometer with a resolution of 2 cm^{-1}. All samples were back-polished to remove the possible SiC grown on the back side of Si substrates before the FTIR measurement. In FTIR spectra, the information of Si substrate was subtracted for comparison.

III. RESULTS AND DISCUSSION

A. Analysis of SiC films

SiC films prepared by heating polystyrene/Si(111) in normal pressure argon atmosphere at different temperatures were investigated by XRD. It was suggested that SiC films can be formed during 1200-1300 °C. In all the films prepared at different temperatures, high-quality and oriented SiC film was obtained at 1250 °C. Figure 1 shows the XRD pattern of the SiC film grown at 1250 °C for 1 h. The peak seen from the pattern at 2θ=35.6° corresponds to the 0.251 nm spacing of close packed planes of silicon carbide. Intensities of other SiC peaks are very weak. This suggests that the SiC film displayed a preferential orientation toward the close packed direction. Rocking curve analysis is used to assess the crystalline quality. Inset in Fig.1 is the rocking curve of the film. The value of full-width at half-maximum (FWHM) of the rocking curve of the film is 1.2°.

XPS measurement was performed on the sample grown on Si substrate after sputtering its surface at different depths with an Ar$^+$ beam, in order to remove the surface oxide and thereby determine the in-depth chemical composition. Figure 2 shows the Si2p XPS spectra of the SiC film grown at 1250 °C for 1 h. In the depth of the SiC layer, the Si2p spectra is well fitted by a single Gaussian line centered at 100.4 eV with a FWHM of 1.6 eV. The component around 100.4 eV is related to the bonding of Si to C atoms. Indeed, such a binding energy is characteristic of Si tetracoordinated

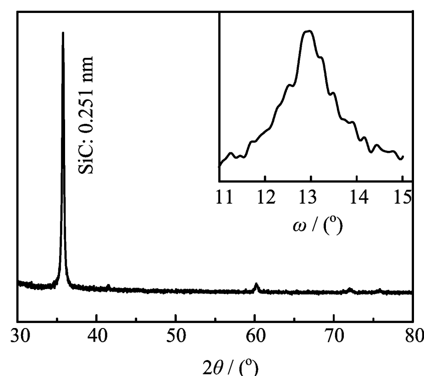

FIG. 1 XRD pattern of the SiC film grown at 1250 °C for 1 h. Inset in the figure is the rocking curve of the film.

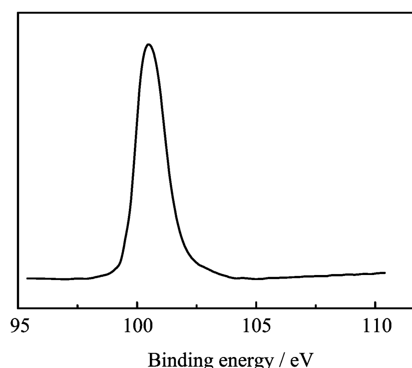

FIG. 2 Si2p XPS spectrum obtained in the depth of the the SiC film grown at 1250 °C for 1 h.

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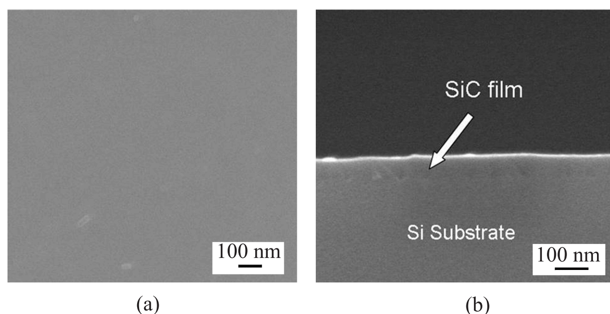

FIG. 3 (a) The planar-view SEM image of the SiC film and (b) the section scan of the SiC film grown at 1250 °C for 1 h.

to C (Si−C4) [20]. The analysis of the Si2p XPS spectra reveals that all the Si atoms present in the film seem to be tetracoordinated to C atoms, confirming the SiC crystallization.

The surface morphology of the as-cleaned SiC film grown at 1250 °C for 1 h was investigated by SEM measurement, as demonstrated in Fig.3(a). The film surface seen from Fig.3(a) is very planar and compact. Figure 3(b) is the image of the cross-section of the film, the SiC/Si interface is very clear, and there are few fault defects because of the escaping of Si atoms on the interface. The thickness of the film in Fig.3(b) is about 60 nm.

The infrared absorption (IR) bands of the SiC films grown at different temperatures are shown in Fig.4. The IR bands reflect the information of films because the signals of Si substrates have been deducted. The major band at 800 cm^{-1} is the characteristic of the stretching mode vibration of Si−C bond in Fig.4. The band shape is an apparently pure Lorentzian form, reflecting a Lorentzian distribution of the Si−C bond lengths and angles [21]. The Lorentz peaks which characterize a fairly crystalline material are due to the transversal optic (TO) absorption of SiC films on Si substrates. SiC plane crystal shows a TO absorption band centered at 794 cm^{-1} [22], which is also a Lorentz peak. The result can be concluded that with temperature increasing the integral area of the Lorentz peaks becomes larger during 1200-1270 °C and decreases during 1270-1300 °C. The film thickness is proportional to the integral area of the Lorentz peak [19]. That is to say, the thicknesses of SiC films first become thicker till 1270 °C and then decrease with further temperature increase.

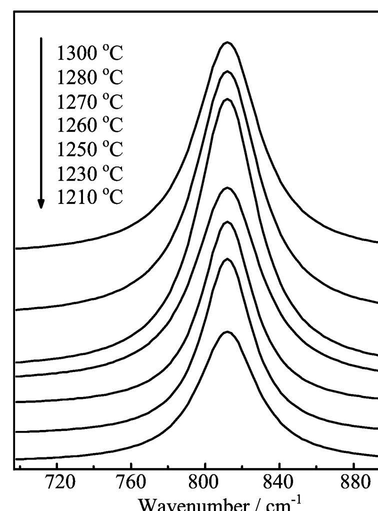

FIG. 4 IR absorption bands of the SiC films grown at different temperatures with signals of Si substrates subtracted.

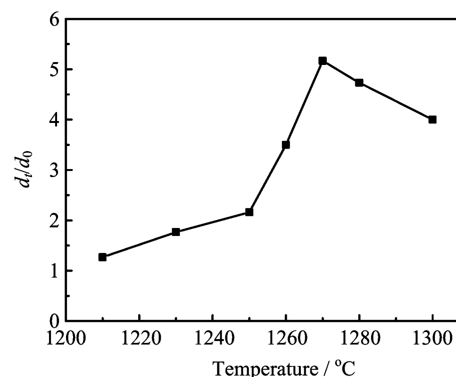

FIG. 5 The relative normalized thicknesses of the SiC films grown for 1 h versus growth temperatures.

B. Growth kinetics of the growth process of SiC films

Mogab has shown a method for determination of the SiC film thickness from the lattice absorption infrared band [19]. Within the first-order approximation, the film thickness d can be obtained from:

$$\int \lg\frac{1}{P}\mathrm{d}v = \frac{4\pi^3\rho\omega_0 d}{2.303} \quad (1)$$

where ω_0 is resonant wave number, P is transmission ratio, $v=\omega/\omega_0$, and ρ is related to the static and high frequency dielectric constant, $\rho=(\varepsilon_0-\varepsilon_\infty)/4\pi$. Therefore, the area of the Lorentz peaks can be obtained from Fig.4 by integration of the Lorentz peaks first. Then, the thicknesses of the SiC films grown at different temperature can be calculated according to Eq.(1). In Fig.5, d_0 is the thickness of the SiC film grown at 1200 °C for 1 h, and d_t is the thickness of the SiC film grown at T (T>1200 °C) for 1 h. We define d_0 as the normalization value, and the thicknesses of the SiC films grown at different temperatures were normalized as d_t/d_0. The relative normalized thicknesses of the SiC films grown for 1 h versus growth temperatures are shown in Fig.5. The sample at 1190 °C is absent in Fig.5 because the absorption band of film grown at 1190 °C is too weak for the relative film thickness, although SiC started to

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grow at this temperature.

The growth rates $K(T)$ of SiC films can be calculated according to the relative normalized thicknesses of the SiC films versus growth temperatures in Fig.5. In the range of 1200-1300 °C, the thicknesses of the SiC films grown for 1 h with increasing growth temperatures have obviously different trends in the three temperature ranges: increasing slowly (1200-1250 °C), increasing quickly (1250-1270 °C), and decreasing (1270-1300 °C). The growth rates $K(T)$ can also be expressed as a function of growth temperatures T by the Arrhenius expression [23]:

$$K(T) = K_0 \exp\left(\frac{-E_a}{k_\mathrm{B}T}\right) \quad (2)$$

where E_a is the apparent growth activation energy, k_B is Boltzmann's constant, and T is the absolute temperature. Therefore, E_a can be obtained from the graph of $\ln K(T)$ *vs.* $1/T$. The apparent activation energies of the growth process of SiC films in the ranges of 1200-1250, 1250-1270, and 1270-1300 °C, were calculated to be 122.5, 522.5, and −127.5 J/mol respectively. Matsunami *et al.* reported 104.5 kJ/mol for β-SiC on silicon substrate in the $SiCl_4$-C_3H_8-H_2 system in the temperature range 1100-1390 °C [24]. Nagasawa and Yamaguchi showed an activation energy of 111.2 kJ/mol for β-SiC on silicon substrate in the SiH_2Cl_2-C_2H_2-H_2 system in the temperature range 1100-1390 °C [25]. The apparent activation energy in the range of 1200-1250 °C agrees with those reported values.

C. Mechanisms of the different growth process

Three kinds of different apparent activation energies of SiC films growth were expressed by three different growth rates, and three kinds of different growth mechanisms were also reflected. Small hydrocarbon molecules arose from pyrogenation of PS at 400 °C. Considering the same volume of the chamber and ambient pressure, the amount of carbon source (small hydrocarbon molecules) arising from pyrogenation of PS can be regarded as the same in such a narrow temperature range (1200-1300 °C). The growth process of SiC films have generally four main stages: rapid formation of a SiC "thermal layer"; transition; thickness increase by diffusion through the "thermal layer"; and apparent end of growth [26]. It is suggested that the film thickness depends on the "diffusion". Obviously, the film thickness increases with increasing growth temperature, due to the increasing diffusion coefficient.

We discuss the growth mechanism of the range 1200-1250 °C first. The growth rate is very slow and the apparent activation energy of this stage is only 122.5 J/mol. The small hydrocarbon molecules formed by heating PS were absorbed on Si substrate at the low temperature at first, then the grains of SiC crystal were formed due to the surface reaction of the small hydrocarbon molecules and Si substrate. The grains of SiC gathered on the surface and grew layer by layer on the Si substrate [27]. The growth process of this stage is a 2D mechanism. During the range of 1250-1270 °C, the diffusion rates of Si atoms became faster with increasing growth temperatures. The Si atoms of Si substrate got across the SiC buffer layer and reacted with the small hydrocarbon molecules on the surface to form SiC film. There were so many SiC grains that they could not grow layer by layer immediately, so many SiC islands appeared on the layer, which is a 3D growth mechanism [28]. The apparent activation energy of this stage is 522.5 J/mol. At the higher temperature of the third stage, the thicknesses of SiC films were decreased by the volatility of Si and C atoms. The apparent activation energy of this stage is −127.5 J/mol, and the growth process of SiC films was controlled by mass transfer and thermodynamics. The thicknesses of SiC films were under the control of the growing and etching of the films.

IV. CONCLUSION

SiC films were prepared by heating polystyrene/Si(111) in argon atmosphere at different temperatures. The XRD pattern of the SiC film obtained at 1250 °C shows that the film displays a preferential orientation toward the close packed direction. The analysis of Si2p XPS spectra reveals that all the Si atoms present in this SiC film seem to be tetracoordinated to C atoms. Planar-view SEM of the SiC film obtained at 1250 °C after RCA cleaning process shows a very planar and compact surface. SiC films were investigated with FTIR spectra. The major band which is an apparently pure Lorentzian form at 800 cm^{-1} is the characteristic of the stretching mode vibration of Si−C bond.

We qualitatively and quantitatively analyzed the FTIR spectra of the samples grown at different temperatures. The thicknesses of the SiC films grown for 1 h had different trends in three temperature ranges: increasing slowly (1200-1250 °C), increasing quickly (1250-1270 °C), and decreasing (1270-1300 °C). The apparent activation energies of the growth process of SiC films in the ranges of 1200-1250, 1250-1270, and 1270-1300 °C, were calculated to be 122.5, 522.5, and −127.5 J/mol respectively. The apparent activation energy in the range of 1200-1250 °C agrees with the reported values.

Mechanisms of the different growth process were investigated. It is suggested that small hydrocarbon molecules arising from pyrogenation of PS were absorbed on Si substrate at first and then reacted with the Si substrate to form a SiC buffer layer. Then, Si atoms in the substrate diffused through the SiC buffer layer and reacted with small hydrocarbon molecules on the surface to form SiC film. In the ranges of 1200-1250 and 1250-1270 °C, the growth process of SiC films were

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controlled by growth kinetics, with 2D and 3D mechanisms respectively. In the range of 1270-1300 °C, the thicknesses of SiC films were decreased by the volatility of Si and C atoms. The growth process of SiC films was controlled by mass transfer and thermodynamics. The thicknesses of SiC films were under the competition of growing and etching of the films. A high-quality and oriented SiC film was obtained at 1250 °C by 2D mechanism, with the FWHM of the rocking curve 1.2°.

V. ACKNOWLEDGMENT

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