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The deposition behavior of SiC:H films deposited using a remote PECVD system with an HMDS precursor and C_2H_2 dilution gas

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Silicon carbide (SiC) is a very attractive material in terms of its mechanical strength, chemical inertness, and other properties for applications in microsystems. SiC:H films were deposited on (100) silicon wafers by a remote plasma enhanced chemical vapor deposition (RPE-CVD) system in the temperature range of 300 °C-450 °C. Hexamethyldisilane (HMDS) and H₂ gas were used as a precursor and a carrier gas, respectively. C_2H_2 dilution gas was used in order to increase the carbon content in the films. The plasma power was varied from 200W to 300W. The stoichiometric and bonding properties of deposited films were investigated by an Fourier transform infrared (FTIR) spectrometer and X-ray photoelectron spectroscopy (XPS). The thickness of deposited films was measured by ellipsometry. The growth rate of SiC:H films decreased with an increase of temperature from 300 °C to 400 °C, however, it increased again at 450 °C. The growth rate of films increased from 0.32 to 0.64, which affected the growth behavior and properties of the films. A higher activation energy and lower potential energy of the sp³ reaction make the sp³ reaction dominant consuming more energy as the deposition temperature was increased. This caused a thickness decrease with an increase of deposition temperature.

Key words: SiC:H, RPE-CVD, HMDS, plasma.

Introduction

Silicon carbide (SiC) has been a very attractive material and an ideal candidate for replacing silicon for many years in micro-electromechanical systems (MEMS) applications due to its superior properties such as high strength, chemical inertness, thermal conductivity, wide bandgap and hardness. However, many difficulties in processing to achieve large and uniform deposition and etching have been an obstacle to commercial use for many years. In recent years, many deposition methods for SiC process including chemical vapor deposition (CVD) [1], sputtering [2], and plasma enhanced chemical vapor deposition (PECVD) [3] have been developed and these silicon carbide materials have been applied in applications for wear-resistance, in high temperature and harsh environments such as for high temperature sensors, engine combustion sensors, etc.

In general, SiC thin films deposited by PECVD at low temperatures show amorphous [4] and hydrogenated properties between organic and inorganic polymers since the source gases are decomposed into complex mixtures of monomers under the plasma and this mixture of monomers react on the substrate at a low temperature. Among PECVD methods, remote PECVD (RPECVD) has a relatively long distance from the plasma generation region to the film deposition area and this reduces the film damage and etching effects caused by energetic ions [5, 6]. It can also make the control of the reaction pathway and composition easier.

In this study, we deposited SiC:H films by a remote PECVD system using an HMDS (hexamethyldisilane) source with C_2H_2 dilution gas in the temperature range of 300 °C~450 °C. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) were used for the analysis of chemical compositions and bonding characteristics.

Experimental

The SiC:H films were deposited on (100) Si wafers by RPECVD using argon gas as the plasma source. The argon plasma was formed by a 13.56 MHz radio frequency plasma generator and plasma matching was controlled by an auto-matching controller. The diameter of the susceptor was 10.16 cm and the susceptor was about 20 cm away from the plasma-active area. HMDS (hexamethyldisilane, $(CH_3)_6Si_2$, 98%, Aldrich) was used as a source and H₂ gas was used as a carrier gas. C₂H₂ gas was introduced as a carbon supplement gas. The flow rate of Ar, H₂ and C₂H₂ gases were controlled by a mass flow controller (MFC) and the flow rate of the HMDS source was controlled by changing the flow

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Fig. 1. Schematic diagram of the showerhead bent source delivery line.

rate of the carrier gas and line pressure. In this study, the flow rate of Ar, H₂, C₂H₂ gases were fixed at 200 sccm, 50 sccm and 3 sccm, respectively. Figure 1 shows a schematic diagram of the bent source line. The source line was shaped as a showerhead bent by an angle of 90 degrees towards the plasma generation area to improve the deposition uniformity. The temperature of the susceptor was increased by a SiC heating element and the actual deposition temperature on the wafer was corrected using a thermocouple. The deposition temperature was varied from 300 °C to 450 °C and the plasma power was varied from 200W to 300W. The deposition time was fixed at 10 minutes. The thickness and refractive indices of films were measured utilizing an ellipsometer (Gaertner L117 C, Helium-neon laser light source, $\lambda =$ 632.8 nm). The relative ratio of silicon, oxygen and carbon in films was measured by XPS. The bonding characteristics of SiC:H films were investigated using FTIR. The crystallinity of the films was analysed by an X-ray diffraction (XRD) method.

Results and Discussions

Figure 2 shows the thickness of deposited films versus the deposition temperature using remote PECVD at plasma powers of 200W, 300W, 400W. These films were identified as amorphous by XRD. Scanning electron microscopy (SEM) observations were performed additionally to ensure the results observed using ellipsometry. Contrary to other CVD process, as the deposition temperature increased, a U-shaped change of deposited thickness appeared. Above a deposition temperature of 300 °C, the deposited film thickness decreased as the deposition temperature increased. However, at 450 °C



Fig. 2. The thickness of deposited films versus the deposition temperature using remote PECVD at various plasma powers with a C_2H_2 flow rate of 3 sccm.



Fig. 3. FTIR spectra of SiC:H films with different deposition temperatures with a plasma power of 300W and a C_2H_2 flow rate of 3 sccm. (a) wavenumbers, 1200-2000 cm⁻¹ (b) wavenumbers, 2500-3400 cm⁻¹.

the deposition thickness increased. The change of deposition mechanism seems to occur between $300 \,^{\circ}C$ and $450 \,^{\circ}C$. In the case of plasma powers of 200W and 400W, the growth behavior has a similar tendency to

that with a plasma power of 300W.

Figure 3 shows the FTIR results at different deposition temperatures. The C-C bonding and C=C bonding were observed at different deposition temperatures and also the alkanes C-H stretching (-C-C-H) and alkenes C-H stretching (-C=C-H) were seen. However, at a deposition temperature of 300 °C, a different tendency was observed. In Fig. 3 (a), the peak at 1250 cm⁻ represents Si-CH₃ bonding and the peak at 1300 cm⁻¹ represents Si-CH=CH₃ bonding. Both peaks were present at 300 °C. However, at other higher temperatures, the Si-CH₃ peak nearly disappeared and there was only the Si-CH=CH₃ peak. This result indicates that the quantity of C=C bonding increases by hydrogen detachment reactions as the deposition temperature changes from 300 °C to 350 °C. The representative reactions in the case of carbon, its heat of formation and activation energy are shown below [7-9]:

 $\begin{array}{ll} sp^{3} \mbox{ carbon creation reaction} & (1) \\ CH_{3}CH_{2}+CH_{3}CH_{2}CH_{3} \rightarrow CH_{3}CH_{2}CH(CH_{3})_{2}+H \\ E_{a}=70.7 \mbox{ kcal/mol}, \ \Delta H=13.4 \mbox{ kcal/mol} \\ sp^{2} \mbox{ carbon creation reaction} & (2) \\ CH_{2}CH_{3} \rightarrow CH_{2}=CH_{2}+H \end{array}$

 $E_a=50.3$ kcal/mol, $\Delta H=40.1$ kcal/mol

The sp² reaction can occur easily since its activation energy is lower than that of the sp³ reaction. However, the enthalpy (Δ H) of the sp² reaction is higher than that of the sp³ reaction and so the sp³ reaction is more stable. This change of carbon creation reaction may affect the changes of deposition thickness and the film characteristics.

XPS narrow scan spectra of C 1s and deconvolution results of C 1s peaks according to Gaussian-Lorentzian distribution at the temperatures of 300 °C and 450 °C are shown in Fig. 4(a) and Fig. 4(b), respectively. There are also other bonds such as the sp³ C-Si bond, however, this is not indicated since the change of the $sp^{3}/$ (sp^2+sp^3) ratio is the focus of this study. The change of the $sp^{3}/(sp^{2}+sp^{3})$ ratio with different deposition temperatures using deconvolution is shown in Fig. 5. The $sp^{3}/$ (sp^2+sp^3) ratio increased from 0.32 to 0.64 as the deposition temperature increased from 300 °C to 450 °C. This indicates that the sp³ creation reaction becomes dominant at higher deposition temperatures above 400 °C. As the deposition temperature increases, higher energy is supplied, however, this higher energy does not make the sp² reaction more activated, but does make the sp³ reaction occur. Sufficient energy to overcome the higher activation energy of the sp³ reaction than that of the sp^2 reaction makes the sp^3 carbon creation reaction occur preferentially since the sp³ bonding has a lower enthalpy than the sp^2 bonding has. In the temperature range of 300 °C-450 °C, much energy is



Fig. 4. C 1s electron orbital XPS deconvolution spectra with temperature changes: (a) T=300 °C, (b) T=450 °C.



Fig. 5. $sp^3/(sp^2+sp^3)$ ratio with different deposition temperatures.

consumed for the sp³ reaction in addition to the sp² reaction. This causes a thickness decrease with an increase of deposition temperature. At 450 °C, the sp³ reaction becomes abruptly dominant and this transition of the reaction mechanism may cause an increase of the deposited thickness at 450 °C compared to the thickness at 400 °C and the sp² and sp³ creation reaction occurs

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Fig. 6. Refractive indices with different deposition temperatures and plasma powers.

by hydrogen detachment reactions [7-9]. In general, as the ratio of the sp^3 bonding increases, the density of the film increases and more dense film is deposited [10, 11]. As the deposition temperature increases, the transition of the reaction mechanism from sp^2 to sp^3 makes the deposited film more dense and this may cause a decrease of film thickness.

Figure 6 shows the refractive indices as functions of both deposition temperature and plasma power. The refractive index increased as the deposition temperature increased and showed no specific relationship with plasma power. Generally, the composition ratio change of sp² and sp³ bonds affects the film density and refractive index and a higher sp³ bond ratio makes the refractive index higher [12]. In addition, as Si-H or C-H bonds increase, the defect density In the film is increased by an increase of meso porosity voids [13] and this causes a lower refractive index. Therefore, the detachment reaction of hydrogen bonds with the sp² and sp³ reactions and a higher sp³/sp² ratio makes the refractive index higher as the deposition temperature is increased and this agrees well with our results shown in Fig. 6.

Conclusions

SiC:H films using an HMDS source and a C_2H_2 dilution gas by a RPECVD method showed different growth rates and chemical bonding characteristics. As the deposition temperature increased from 300 °C to 400 °C, the deposition rate decreased continually but

increased at a temperature of $450 \,^{\circ}$ C. It was revealed that Si-CH₃ bonds disappeared and the quantity of C=C bonding increased by hydrogen detachment reactions as the deposition temperature changed from 300 °C to $350 \,^{\circ}$ C. The sp³/(sp²+sp³) ratio increased as the deposition temperature increased and this ratio of carbon creation reactions by hydrogen detachment reactions affects the deposition thickness. These results were again ascertained by comparing refractive indices at several deposition temperatures.

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