

Characterization of SiC:H films deposited using HMDS precursor with C₂H₂ dilution gas by remote PECVD system

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Amorphous SiC:H films were deposited on (100) silicon wafer by remote-Plasma Enhanced Chemical Vapor Deposition system in the temperature range of 400°C–450°C. Hexamethyldisilane (HMDS) and C₂H₂ gas were used as a precursor and a dilution gas, respectively. The lower deposition temperature and lower sp³/sp² carbon bonding ratio made lower dielectric constant.

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1. Introduction

Recently, many deposition methods for SiC processes, including CVD,¹⁾ sputtering,²⁾ and PECVD,³⁾ have been researched and developed by various research groups. In general, SiC thin films deposited by plasma enhanced chemical vapor deposition (PECVD) at low temperatures show amorphous⁴⁾ and hydrogenated properties in between the properties of organic and inorganic polymers, since source gases are decomposed to complex mixtures of monomers under plasma which react on the substrate at low temperatures. This is known as plasma polymerization, and this phenomenon is a general characteristic of films deposited by PECVD.⁵⁾ The amorphous and polymeric SiC film deposited by PECVD contains some hydrogen and oxygen in the film, which allows the possibility of using SiC films deposited by PECVD in low-k applications.^{6),7)} The most commonly used low-k material, fluorosilicate, has a k-value of 3.5, which is slightly lower than SiO₂. In order to reduce the RC delay time, more low-k materials with k-values less than 2 must be introduced. SiC deposited by PECVD is a potential candidate as a low-k material. Among the PECVD methods, the remote PECVD (RPECVD) method has a relatively long distance from the plasma generation region to the film deposition area causing film damages and etching effects caused by a decrease of energetic ions.^{8),9)} Using remote PECVD has advantages of easy control of reaction pathway and composition. In this study, we deposited SiC films by a remote PECVD system using HMDS (hexamethyldisilane) as a source and C₂H₂ as a dilution gas under various deposition temperatures, plasma powers, and dilution gas flow rates. X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) were used for the analysis of chemical compositions and bonding characteristics.

2. Experimental

The SiC films were deposited on (100) Si wafers by RPECVD using argon gas as the plasma source. Argon plasma was formed by a 13.56 MHz RF plasma generator, and plasma matching was controlled by an auto-matching controller. The diameter of the susceptor was 4 inches, and the susceptor was about 20 cm away

from the plasma generation region. HMDS (hexamethylsilane, (CH₃)₆Si₂, 98%, Aldrich) was used as the source and H₂ gas was used as a carrier gas for the bubbled HMDS source. C₂H₂ gas was used as a dilution gas for carbon supplementation and controlling the carbon ratio in the film. The flow rates of the 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 rate of the carrier gas and line pressure. In this study, the flow rates of Ar and H₂ gases were fixed at 200 sccm and 50 sccm, respectively. The source line was shaped as a shower head with an angle of 90°C toward the plasma generation region to improve deposition uniformity. A SiC heating element was used to increase the temperature of the susceptor, and the actual deposition temperature on the wafer was corrected using a thermocouple. The deposition temperatures used were 400 and 450°C. The flow rate of C₂H₂ was varied from 3 sccm to 200 sccm to investigate the effect of the carbon ratio on the dielectric constant. The plasma powers used were 200 and 300 W. The relative ratios of silicon, oxygen, and carbon in the films were measured using X-ray photoelectron spectroscopy (XPS, VG Scientific, ESCALAB 220i-XL) and auger electron spectroscopy (AES, Physcial Electronics, PHI680 Auger Nanoprobe). The dielectric constant of the film was calculated through C-V analysis using a Keithly 590 C-V analyzer at 1 MHz.

3. Results and discussions

Figure 1 shows the XRD analysis data of the SiC film deposited at 450°C and 300 W with a C₂H₂ flow rate of 3 sccm. The XRD analysis results showed that the deposited film was amorphous. In the XRD analysis, all of the samples deposited under the various deposition conditions showed amorphous states. The complex mixtures of decomposed monomers under plasma react on the substrate and cause amorphous SiC film deposition. It is known that amorphous SiC, which contains some hydrogen and oxygen in the film, is highly crosslinked with each other and forms a random network structure with hydrocarbon groups (-CH_n).^{6),7)} **Figure 2** shows the dielectric constants at different deposition temperatures of 400 and 450°C. As the deposition temperature was increased, the sp³ carbon bonding ratio and the dielectric constant increased. In our previous works,^{10),11)} we showed that the sp³ carbon bonding ratio increased as the deposition temper-

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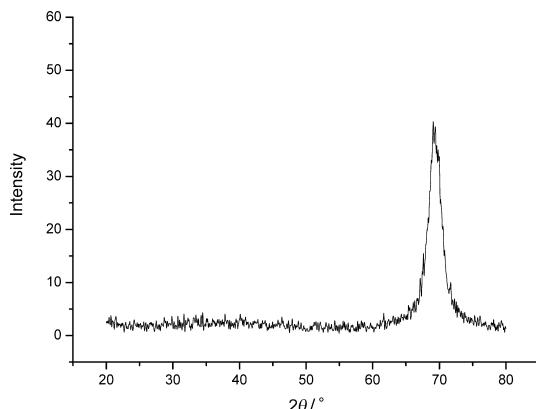


Fig. 1. XRD analysis data of the SiC film deposited at 450°C with a plasma power of 300 W and a C₂H₂ flow rate of 3 sccm.

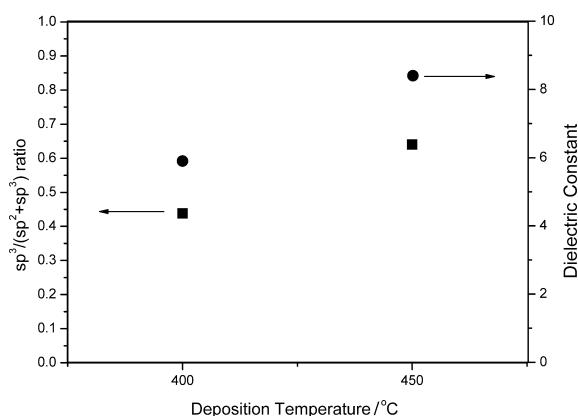


Fig. 2. Dielectric constant at deposition temperatures of 400 and 450°C with a plasma power of 300 W and a C₂H₂ flow rate of 3 sccm.

ture increased. The sp^3 carbon bonding ($E_a = 70.7$ kcal/mol, $\Delta H = 13.4$ kcal/mol) has a higher activation energy than sp^2 carbon bonding ($E_a = 50.3$ kcal/mol, $\Delta H = 40.1$ kcal/mol). Therefore, the sp^2 reaction can occur more easily since its activation energy is lower than that of the sp^3 reaction. However, the enthalpy (ΔH) of sp^3 carbon bonding is lower than that of sp^2 carbon bonding. Therefore, the sp^3 reaction is more stable if sufficient energy (greater than the activation energy of sp^3) is supplied at higher deposition temperatures. As shown in Fig. 2, sp^3 bonding became dominant at 450°C, as compared to 400°C. In other studies,^{12),13)} an increase of the sp^3 bonding ratio resulted in increased film density, and a denser and harder film is deposited. Denser and harder films lead to an increase in the dielectric constant of the film. Also, as sp^3 bonding increases, the Si–H and C–H bonds decrease due to bonding to each other to produce sp^3 bonding. The increase of Si–H and C–H bonds leads to an increase in defect density and porosity in the film caused by an increase of meso porosity voids.^{7),15)} Therefore, the dielectric constant increases as the deposition temperature increases, since a denser and harder film is deposited due to the increase of sp^3 bonding. **Figure 3** shows the dielectric constants and carbon concentrations as a function of the C₂H₂ flow rate. As the C₂H₂ flow rate increased, the carbon concentration in the film increased. The C₂H₂ dilution gas is a carbon supplement gas for SiC film deposition, and the flow rate of C₂H₂ gas determines the carbon ratio in film. As shown in Fig. 3, the dielectric constant decreased as the C₂H₂ flow rate increased. However, the dielec-

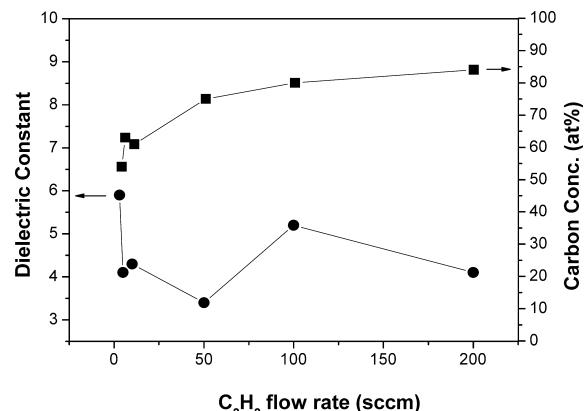


Fig. 3. Dielectric constant and carbon concentration as a function of C₂H₂ flow rate at a deposition temperature of 400°C and a plasma power of 300 W.

tric constant increased at a C₂H₂ flow rate of 50 sccm. Studies of low- k materials such as SiOC and hydrogenated SiC have determined that an increase in hydrocarbon groups leads to a porous network structure resulting in a decreased dielectric constant.^{7),14)} As the C₂H₂ flow rate is increased, hydrocarbon related groups (–CH_n) increase in the film resulting in a decreased dielectric constant. However, as shown in the carbon concentration results in Fig. 3, the carbon concentration is saturated at C₂H₂ flow rates over 50 sccm. We showed that the C–C bonding and sp^3 carbon bonding increase as the C₂H₂ dilution gas flow rate is increased in our previous reports.¹⁰⁾ Saturated carbon particles react with each other under high energy at a plasma power of 300 W, and carbon related bonding such as C–C bonding and sp^3 carbon bonding increase in the film. This increase in carbon related bonding, such as sp^3 bonding, causes an increase in the dielectric constant. In other studies utilizing PECVD SiC,^{6),7)} an a-SiC:H film deposited using PECVD showed an amorphous and polymeric state. The additional energy and modified ratio of radicals cause the properties of carbon related groups to change.^{10),11)} Since the carbon in the film exists in the form of CH_n groups, this change in the carbon related groups affects the density, refractive index, hardness, and other film properties. Therefore, changes of not only the C₂H₂ flow rate but also the plasma power causes changes of the carbon related bonding type and carbon ratio. This leads to changes of the dielectric constant. **Figure 4** shows the dielectric constant at different C₂H₂ flow rates and plasma powers. The dielectric constant of the film deposited at a plasma power of 200 W was lower than that deposited at 300 W. As the plasma power is increased, the decomposition of source and dilution gases becomes easier and decomposed monomers react under the high plasma power. The increased energy at high plasma power produces strong and dense bonding, such as sp^3 bonding, Si–C, and C–C bonding, since the amount of decomposed radicals increases and radicals become more reactive at high plasma power. Therefore, as the plasma power increased, the dielectric constant increased since the increase of strong dense bonding produced denser deposited films. At the plasma power of 300 W, the dielectric constant increased at C₂H₂ flow rates over 50 sccm due to the saturated carbon reaction, as shown in Fig. 3. However, at the plasma power of 200 W, the dielectric constant was similar or even lower at C₂H₂ flow rates over 50 sccm. At a plasma power of 300 W, higher energy is supplied. This increased energy for strong bonding and the sufficient supply of saturated carbon at

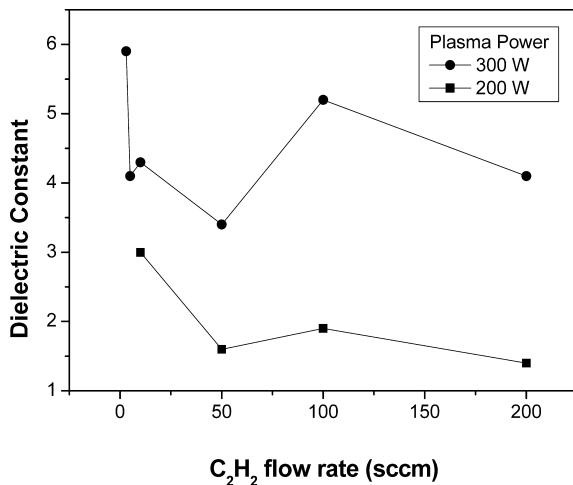


Fig. 4. Dielectric constant at different C₂H₂ flow rates and plasma powers at a deposition temperature of 400°C.

C₂H₂ flow rates over 50 sccm leads to increased strong and dense bonding, such as sp³ bonding. At a plasma power of 200 W, the low plasma power causes the ratio of CH_n-like radicals to increase in the decomposed monomer, and the energy of the plasma power is insufficient for strong bonding such as sp³ carbon and C-C bonding. Also, the amount of decomposed radicals under a plasma power of 200 W is less than that under a plasma power of 300 W. The increase of the C₂H₂ flow rate above 50 sccm causes the carbon ratio in the film to increase, and this increase in carbon bonding corresponds to increases in hydrocarbon and sp² carbon bonding in the film since fewer radicals and the low plasma power are insufficient for sp³ carbon bonding. In other research regarding carbon bonding,^{16,17)} sp² carbon bonding had the tendency to generate clusters rather than existing randomly in an amorphous matrix. These clusters make a ring or chain structure and bond to other carbon or hydrogen atoms around the cluster. In particular, the clustering of ring structures in the film increases as the ratio of sp² bonding increases. The increase in ring and chain structures caused by an increase in sp² bonding results in a more porous film. Also, Si-H and C-H bonds, which exist more with a plasma power of 200 W than in the film deposited at a plasma power of 300 W, make the deposited film more porous. Therefore, the increase in hydrocarbon and sp² bonding under the insufficient plasma power of 200 W leads to a decrease in the dielectric constant as the C₂H₂ flow rate increased from 50 sccm to 200 sccm. Consequently, an amorphous SiC film with a dielectric constant under 2 can be achieved by deposition at a low plasma power of 200 W and a higher flow rate of C₂H₂ dilution gas. The deposition temperature, plasma power, and flow rate of dilution gas affected the dielectric constant of the film.

4. Conclusion

We deposited amorphous SiC films on (100) Si wafers by remote PECVD using HMDS and C₂H₂ gas as precursor and dilution gases, respectively. The deposition conditions, including temperature, plasma power, and C₂H₂ flow rate, were varied to investigate the effect of deposition conditions on the dielectric constant. As the deposition temperature increased, sp³ carbon bonding occurred more frequently, causing an increase in the dielectric constant. At the high plasma power of 300 W, the dielectric constant decreased up to a C₂H₂ flow rate of 50 sccm and increased at C₂H₂ flow rates above 50 sccm. As the plasma power decreased, the dielectric constant decreased, and a dielectric constant under 2 was achieved at a low plasma power of 200 W and C₂H₂ flow rates above 50 sccm.

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