

The changing behavior of the dielectric constant of a-SiC:H films deposited by remote PECVD with various deposition conditions using HMDS and PPCS

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a-SiOC:H films were deposited by a remote PECVD (Plasma Enhanced Chemical Vapor Deposition) system using HMDS (Hexamethyldisilane) and PPCS (Polyphenylcarbosilane) as the precursor. PPCS precursor was synthesized using a Kumada rearrangement at 350 °C by KICET (Korea Institute of Ceramic Engineering and Technology). We compared the properties of film deposited using PPCS with that deposited using HMDS. H₂ gas and C₂H₂ gas were used as the carrier gas and dilution gas, respectively. The deposition temperature was varied between 100 °C-250 °C. The flow rate of the H₂ carrier gas was varied from 3 to 100 sccm for a study of the deposition conditions which effects the film stoichiometry and dielectric constant of deposited films. The thickness of deposited films was measured by ellipsometry and the dielectric constant was examined by C-V measurements of deposited films. Using both sources without a C₂H₂ dilution gas led to the deposition of SiO₂ films. The depositions using the C₂H₂ dilution gas caused a change of the carbon ratio and carbon hybridized bonds which play an important role in the change of the dielectric constant.

Key words: HMDS, SiC, PPCS, dielectric constant, PECVD.

Introduction

Silicon carbide has been researched as an ideal compound of silicon for many years due to its mechanical strength, chemical inertness, thermal conductivity and other superior properties. However many difficulties in processing to large and uniform depositions and etching have been barriers to commercial applications. Recently, many processes for SiC deposition including CVD, sputtering and PECVD have been developed [1-3]. Among these deposition methods, SiC deposition using remote PECVD has been researched because this method can reduce the deposition temperature of SiC films and the damage caused by a plasma [4, 5]. Also, the application of a-SiC:H films deposited by remote PECVD for low-k material has been researched because of their mechanical strength and resistance against moisture. In general, SiC films deposited by PECVD with a low deposition temperature show amorphous and hydrogenated properties between the organic and inorganic polymer since monomers decomposed under the plasma are deposited as mixed states of decomposed monomers on the substrate at a low temperature [6]. This is called plasma polymerization and this phenomena is a general characteristic of films deposited by PECVD [7]. This polymerization of deposited SiC films can lead to lower dielectric constants, under 2.0. Therefore, deposition of SiC films using remote PECVD

can lead to lower dielectric constants under 2.0 while maintaining their superior mechanical strength, chemical inertness and resistance against moisture. Also, these SiC films can be an excellent diffusion barrier against copper in the damascene process.

In this study, a-SiC:H films were deposited by a remote PECVD system using HMDS and PPCS as the precursors. The PPCS precursor is newly synthesized using a Kumada rearrangement at 350 °C by KICET. HMDS is widely used as a source for a-SiC and PPCS has a higher carbon content as a source. We established the deposition conditions of PPCS for remote PECVD and compared the properties of a film deposited using PPCS with that deposited using HMDS. H₂ gas and C₂H₂ gas were used as the carrier gas and dilution gas, respectively. The deposition temperatures were 200 °C and 400 °C. The flow rate of H₂ gas was varied from 0 to 100 sccm to establish deposition conditions for PPCS. The thickness of deposited films was measured by ellipsometry and the dielectric constant was examined by C-V measurements of deposited films.

Experiments

The amorphous and hydrogenated SiC films were deposited on (100) Si wafer by remote PECVD using argon gas as the plasma source. The argon plasma was formed by a 13.5 MHz RF plasma generator and plasma matching was controlled by an auto matching controller. The diameter of the susceptor was 4-inches (100 mm) and the susceptor was about 20 cm from the plasma generation region. HMDS (hexamethyldisilane, Aldrich) and PPCS

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(polyphenylcarbosilane, KICET) were used as sources for SiC deposition and a carrier gas for the bubbled source was H_2 . C_2H_2 gas was used as a dilution gas for carbon supplement and to control the carbon ratio in the film. The flow rate of Ar, H_2 , C_2H_2 gases were controlled by a mass flow controller (MFC) and the flow rate of HMDS and PPCS sources was controlled by changing the flow rate of carrier gas and the line pressure. In this study, the flow rate of Ar and C_2H_2 were fixed at 200 sccm and 10 sccm, respectively. The flow rate of H_2 gas was varied between 0 and 100 sccm to establish deposition conditions for the PPCS source. The source line was shaped as shower head bent by an angle of 90 degrees toward the plasma generation region to improve the deposition uniformity and decomposition of gas species. A SiC heating element was used to increase the temperature of the susceptor and the actual deposition temperature on the wafer was corrected using thermocouple. The deposition temperatures were 200 °C and 400 °C to investigate the effect of the thermal effect on the dielectric constant of the film. The plasma power was varied from 200 W to 400 W to investigate the effect of the plasma power on deposition condition. The deposition thickness of the film was investigated using a Gaertner L117 C Ellipsometer using helium-neon laser ($\lambda = 632.8$ nm). The relative ratios of silicon, oxygen and carbon in the films were measured using X-ray photoelectron spectroscopy (XPS, VG Scientific, ESCALAB 220i-XL). The dielectric constant of films was calculated through a C-V analysis using a Keithly 590 C-V analyzer at 1 MHz.

Results and Discussions

Fig. 1 shows a XPS wide scan spectrum of a film deposited using a PPCS source without C_2H_2 dilution gas at the deposition temperature of 400 °C and plasma power of 400 W. The XPS wide scan shows that the deposited film without the C_2H_2 dilution gas is SiO_2 . The atomic concentrations of C, O and Si were 5.33, 64.71 and 29.77, respectively. The small composition of carbon seems to originate from a small amount of CH_n group and con-

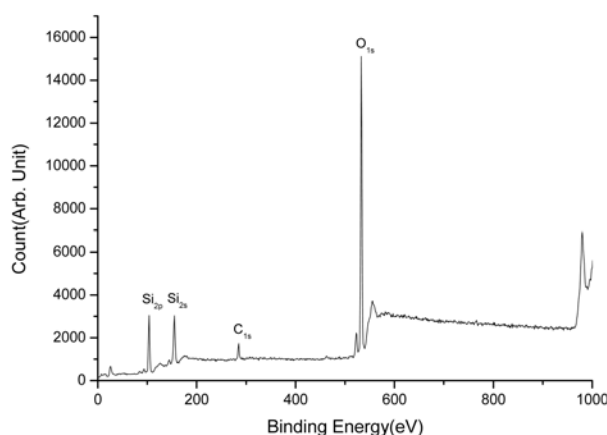


Fig. 1. XPS wide scan spectrum of a film deposited using a PPCS source without C_2H_2 dilution gas ($T = 400$ °C and PP = of 400 W).

taminating carbon. At other deposition temperatures and plasma powers, the composition of deposited films using only PPCS without the C_2H_2 dilution gas was SiO_2 . In our research [8], SiO_2 films were formed when deposited without the C_2H_2 dilution gas with various deposition conditions. The carbon concentration of the film deposited using HMDS without C_2H_2 dilution gas was below 5%. Compared with the result of deposition using HMDS, the result of deposition using PPCS without C_2H_2 dilution gas shows that both liquid precursors do not behave as a carbon supplement source but as silicon supplement source in the film. It seems that the amount of hydrocarbon gas which is needed to initiate plasma polymerization is too small. In other research about plasma polymerization [9], the process initializing plasma polymerization related with carbon needs hydrocarbon radicals, especially broken C-H bonds, to promote the chain polymerization. Without the C_2H_2 dilution gas, there is a small amount of hydrocarbon and this amount is not enough to fully-activate the chain reaction to make the source become radical. Therefore, a small amount of excited oxygen in the chamber preferentially reacts with Si under plasma conditions and this leads to deposition of SiO_2 films.

Fig. 2 shows the change of deposition thickness using a PPCS source and C_2H_2 dilution gas as a function of deposition time compared with the result using a HMDS source with C_2H_2 dilution gas. In Fig. 2, there are critical times for the deposition in both cases for HMDS and PPCS. It is known that the crosslinker of the silyl (Si-H) group is initiated in the first stage of deposition [10]. Also, deposition of a polymeric film in the plasma is based on the attachment of the chemically-activated species generated in the plasma before. In our study, we used a remote PECVD system to deposit films. In our deposition system, the plasma generation area is separated from the deposition area and the source with the dilution gas flows to the area between the plasma and susceptor. Therefore, it needs time

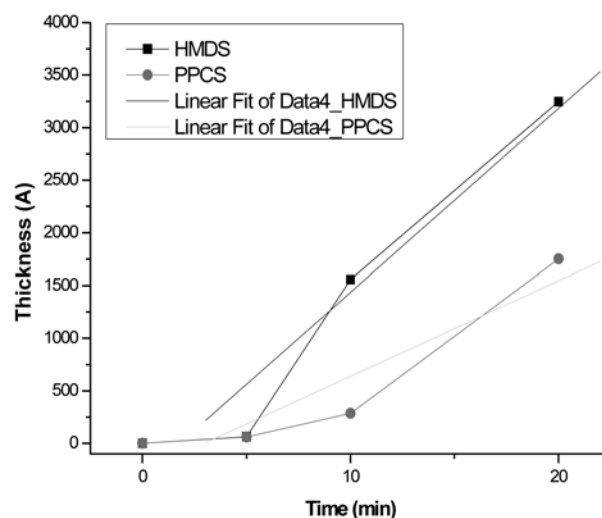


Fig. 2. Deposition thickness using PPCS and HMDS sources with C_2H_2 dilution gas as a function of deposition time.

for the plasma reaction and decomposition of the source and dilution gas after activation of the argon plasma. In this mechanism, it needs a critical time for deposition and the deposition thickness increases proportionally after this critical time. In the case of deposition using HMDS, the deposition thickness was under 100 Å before 10 minutes deposition time and increased after 10 minutes deposition time. However, in the case of deposition using PPCS, the deposition thickness increases after 20 minutes deposition. The deposition thickness of the film using PPCS for 20 minutes was similar to that using HMDS for 10 minutes. It seems that this difference is caused by the molecular weight of the source. The molecular weight of HMDS is about 145 and that of PPCS is between 250 and 300. Because of the heavier molecular weight, less PPCS source is transferred than HMDS with the same flow rate of carrier gas. Therefore, in our study, we will compare the properties of films deposited for a critical time since the deposition of films becomes stable after the critical time.

Fig. 3 shows the deposition thickness change of films deposited using HMDS and PPCS sources as a function of plasma power and the flow rate of the carrier gas. In Fig. 3(a), the deposition thickness decreases as the plasma power decreases in both cases using PPCS and HMDS. As the plasma power increases, more energy is supplied which decomposes the gas species. This leads to an increase of the reactive radicals and makes more reactive radicals. This increase in radical generated and greater reactivity makes the deposition thickness increase as the plasma power is increased. However, no film was deposited at 200 W using the PPCS source. PPCS is a molecule with a larger size which has the structure of $(\text{Si-C}_6\text{H}_6\text{-CH}_2\text{-H})_n$ and chain-like links of this. Therefore, it needs more plasma

power to make more radicals and to activate the plasma reaction. At a plasma power of 300 W, in spite of the longer deposition time, less film using PPCS was deposited than using HMDS. At a plasma power of 400 W, the deposition thickness using PPCS increased dramatically in spite of the longer deposition time of 20 minutes than that of 10 minutes using HMDS. When a high enough plasma power to activate the plasma reaction of PPCS was supplied, the deposition thickness increased after the critical time for deposition. However, 400 W of plasma power is a high power for a plasma in even a remote plasma system and it can lead to damage of the deposition system and the plasma matching box. More research is needed to decrease the plasma power for deposition and further research on this aspect is ongoing.

Fig. 3(b) shows the change of deposition thickness as a function of the flow rate of carrier gas using a PPCS source after a deposition time of 20 minutes. At a plasma power of 200 W, a film was hardly deposited in spite of changing the flow rate of the carrier gas. The deposition thickness of a film with a flow rate of 100 sccm carrier gas was about 200 Å and no film were deposited under a flow rate of 200 sccm carrier gas. At a plasma power of 400 W, the deposition thickness increased as the flow rate of the carrier gas increased from 30 sccm to 50 sccm and the deposition thickness decreased as the carrier gas flow rate increased from 50 sccm to 100 sccm. As the flow rate of carrier gas increases, more PPCS can be transferred to the chamber. Under a low plasma power state, a greater supply of the source leads to an enhanced plasma reaction since the plasma power is not sufficient to make more radicals for the plasma reaction and a greater supply of the source makes a possibility of a reaction of the source with less

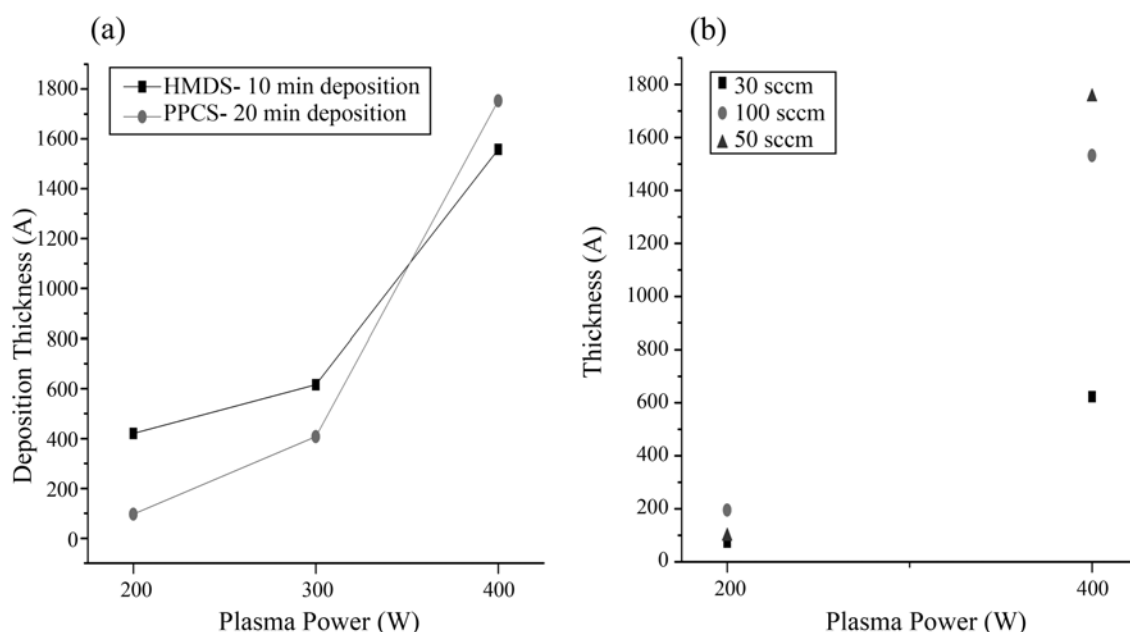


Fig. 3. Deposition thickness change of films deposited using HMDS and PPCS sources as a function of (a) plasma power and (b) flow rate of carrier gas.

existing radicals increase. At a plasma power of 400 W, plasma power is enough to make more activated radicals exist and an activate plasma reaction. Therefore, as the flow rate of carrier gas increases from 30 sccm to 50 sccm, the deposition thickness increase since more source was supplied under the plasma which were enough to fully react with radicals. However, as the flow rate of carrier gas increased from 50 sccm to 100 sccm, the deposition thickness decreased. This seems to be caused by the interference of hydrogen with C-H_n bonds. Other research about a-SiC:H reports that at a higher hydrogen concentration, a low availability of Si leads to Si-C bonds. However, they also report the carbon incorporated forming C-H bonds decreased [11]. As we show in the explanation of Fig. 1, the attachment of hydrocarbon and broken C-H bonds mainly contribute to the plasma polymerization. At a flow rate of the carrier gas of 100 sccm, too much hydrogen exists in the plasma and this leads to a decrease of C-H related bonds in the film which is related with carbon incorporation in the film and cross-linking with other CH_n groups. Therefore, the deposition thickness of film decreased with a top high flow rate of carrier gas.

Fig. 4 shows atomic concentrations and dielectric constants of films deposited at a deposition temperature of 200 °C and plasma power of 400 W. The dielectric constant of the film using the HMDS source was referred from our previous report [12]. Using the PPCS source, the carbon content decreased and the silicon and oxygen contents increased compared with the film using the HMDS source. The PPCS source has the chemical formula (Si-C₆H₆-CH₂-H)_n which contains a benzene ring. These benzene rings are very stable and can not be broken easily compared with other CH_n groups. Therefore, the benzene ring remains as the chain plasma reaction proceed due to radicals at the deposition benzene rings remain in the deposited film. This benzene ring does not crosslink with other CH_n groups and interfere in reactions related with C-H bonds and radicals. Therefore, the carbon content of deposited films using the PPCS source become less than that using the

HMDS source.

In Fig. 4, the dielectric constant of the film deposited using PPCS was 3.7, rather higher than that using HMDS. At the deposition temperature of 200 °C using the HMDS source, the change of carbon bonding from CH_n bonding to sp² bonding which is caused by the thermal energy of the deposition temperature affects the structure of the film [12]. In other research about carbon bonding [13, 14], sp² carbon bonding tends to generate a cluster rather than exist randomly in an amorphous matrix. These clusters which form sp² bonding make a ring or chain structure and bond to other carbon or hydrogen atoms around the cluster. The clustering of ring structures in the film increase as the ratio of sp² bonding increases. Therefore, the increase of ring and chain structures caused by an increase of sp² bonding results in more porous films and leads to a decrease of the dielectric constant as the deposition temperature increases. However, in the deposition using the PPCS source, the remaining benzene rings interfere thus changing the reaction to sp² bonding since the thermal energy is not enough to break benzene ring. Also, these benzene rings interfere in the crosslink is between the CH_n groups and making the networking structure. This leads to an increase of dielectric constant which is deposited using the PPCS source.

Conclusions

Amorphous and hydrogenated SiC films were deposited using HMDS and PPCS sources with a C₂H₂ dilution gas by remote PECVD under various deposition conditions. The deposition behavior of the film using the PPCS source showed different properties compared with the film deposited using the HMDS source. The critical time for deposition using the PPCS source was 20 minutes which is longer than that using the HMDS source. At a low plasma power, no film was deposited using the PPCS source. However, at a high plasma power, a-SiC:H film was deposited using the PPCS source after a critical time. The PPCS source has a benzene ring in the source and this benzene ring remains in the deposited film. This leads to decrease of the carbon content in the film and an increase of the dielectric constant of the film using the PPCS source.

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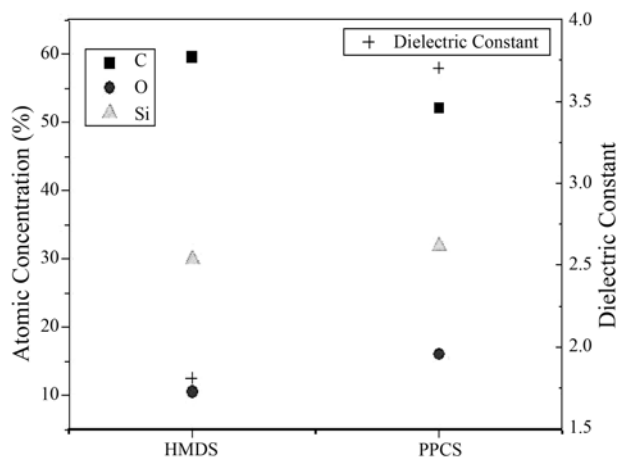


Fig. 4. Atomic concentrations and dielectric constants of deposited films (T = 200 °C and PP = 400 W).

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