

CVD에 의한 비정질불화탄소 박막의 유전상수의 열처리 의존성

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Dependence of Dielectric Constant of the Fluorinated Amorphous Carbon Films on Annealing Film by using CVD

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ABSTRACT

Fluorinated amorphous carbon films were deposited by using an inductively coupled plasma chemical vapor deposition with mixture of carbon tetrafluoride(CF₄) and methane(CH₄) gases. The chemical bonding structure was also characterized by using X-ray photoelectron spectroscopy. a-C films such as a-C:H films or a-C:F films is termed amorphous carbon or diamond like carbon, because of their bond structure similar amorphous silicon. The structure is confirmed from sp³ carbon spectra of polycrystalline diamond by using X-ray photoelectron spectroscopy. Fluorinated amorphous carbon films consist of the bonding structure with the sp³ carbon. The bonding structure consisted of sp³ carbon means partial cross link or cross link which improve the adhesion and hardness. The balanced cross link structure of a-C:F films decrease the dielectric constant and also improve the mechanical properties because of good adhesion and hardness like diamond.

Key Words : fluorinated amorphous carbon films, cross link, C-H hydrogen bond, sp³ carbon.

1. INTRODUCTION

To get high-speed integrated circuits, new inter-metal dielectric materials are required instead of thermal silicon-dioxide films. These low-k mate-

rials are fluorine-doped silicon dioxide films(SiOF), hydrogenated amorphous carbon films(a-C:H), fluorinated amorphous carbon films(a-C:F) and organic-inorganic hybrid silica films(SiOC) [1-8]. a-C often termed diamond like carbon(DLC). These materials are hydrogenated amorphous carbon films (a-C:H) and Fluorinated amorphous carbon films (a-C:F). These films consists of two components, that is, diamond(sp³ bonded carbon) and nondiamond which depends strongly on the preparation conditions, influences the physical and chemical

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properties of a-C films. Atomic oxygen generated by electron impact dissociation is known to remove the nondiamonds component. But the atomic structure of such DLC is not well understood. Carbon holds a special fascination for scientists of many fields because of the great diversity of structural and electronic properties exhibited by its many field. a-C(amorphous carbon) films represent large variation in structure as a function of temperature and various preparation condition as grown due to C-H hydrogen bonds. C-H hydrogen bonds occurs inductive effect by the electron distribution in condition of neighbor high electronegative atoms or double bonds in atomic structures disordered forms of a-C films are particularly attractive as films with semiconducting properties related to graphite yet with hardness more like diamond. The similarity of its properties to diamond suggests the possibility that all carbon atoms are tetrahedrally bonded and that the electrons of the carbon are therefore in an sp^3 configuration. In this model, we expect a random network structure similar to that of amorphous silicon[9-15]. The sp^2 , sp^3 carbon in a-C films are obtained by Raman spectroscopy, FT-IR(Fourier transform infrared) spectroscopy, and X-ray photoelectron spectroscopy(XPS). The C 1s electron orbital spectra by using XPS were decomposed into graphite(284.1(eV), sp^2 carbon) and diamond(285.5(eV), sp^3 carbon), which data were obtained from the spectra of polycrystalline diamond(pc-diamond) and crystalline graphite(c-graphite) samples[16]. In this study, the relationship between the dielectric constant and the fluorine in a-C:F films as low-k materials is researched. The variation of the bonding structure according to the flow rate ratio is analyzed by using XPS and the reason for the variation of bonding structure is also studied.

II. EXPERIMENT

Fluorinated amorphous carbon films were deposited on a p-type(100) substrate by using an inductively coupled plasma chemical vapor deposition with mixture of carbon tetrafluoride(CF_4) and methane(CH_4) gases for 10 minutes. a-C:F films were deposited with different flow rate ratio of CF_4 : CH_4 respectively, but the total flow rate was kept at 40 sccm. High density plasma about 10^{12} cm^{-3} was obtained at low pressure with rf power of 800 W, and the base pressure of $\sim 10^{-6}$ Torr was obtained for each experiment. The thickness of the deposited a-C:F films were measured by an ellipsometer. The dielectric constant was also investigated using a MIS(Al/a-C:F/p-Si) structure. The chemical properties of a-C:F films was researched according to variation of the CH_4/CF_4 flow rate ratio because the concentration of radicals change due to the gas flow rates. The effect of annealing in a-C:F films as done with various temperature by N_2 ambient post heat treatment in an vacuum. The chemical bonding structure was also characterized by using X-ray photoelectron spectroscopy(XPS, ESCALAB250, VG Scientifics, UK). The pressure of the analysis chamber was maintained at 5.0×10^{-8} Torr during each measurement with charge compensation with flood gun. The X-ray source was Al K line(1486.6 eV) operating at 150 W. Survey spectrum was obtained in the range of 1 to 600 eV by using 1 eV scan step size with 50 eV pass energy but high resolution spectra for the individual element was collected with a scan step size of 0.05 eV with 20 eV pass energy.

III. RESULT AND DISCUSSION

Figure 1(a), (b) and (c) show C 1s electron

orbital spectra of the as-deposited films with the variation of the flow rate ratio. The XPS narrow scan spectra of the C 1s peaks of as-deposited films were deconvoluted by fitting the data with a number of Gaussian peaks. The fitted results for the as-deposited films show that C 1s spectra consist of major peaks centered at approximately 286 eV. The values of C 1s spectra of a-C:F films mean the peak of sp^3 carbon in the spectra of polycrystalline diamond. The main peaks of C 1s spectra are 286.4 eV, 286.8 eV and 287.5 eV according to increasing the fluorine flow rate, relatively. The bonding strength of films according to increasing the fluorine flow rate increases, and shows low energy distribution of cross link structure such as weak interaction between atoms. a-C:F films consist of alkyl group and the electronegative atom such as the F radicals dissociated from the CF_4 . The chemical shift of proton is described by the inductive and resonance stabilization due to the variation of the electron distribution. In the inductive stabilization, high electronegative atom draws the electron density through σ bonding therefore total electron density becomes low. On the other hand, alkyl group in the resonance stabilization supplies the electron density through π bonding, and then the electron density becomes high. Compound due to the electrophilic aromatic substitution through σ bonding and C-C double bonding with π bond is sp^3 hybrid carbon consisted of two σ bonds and one π bond.

$$H_{eff} = H_0 - \alpha H_0 \quad (1)$$

H_{eff} is effective magnetic field intensity, H_0 is external stable magnetic field intensity for nuclear resonance, the resonance frequency (ν) of the proton is

$$\nu = \frac{\gamma}{2\pi} H_0 (1 - \alpha) \quad (2)$$

where α is Abschirmungskonstante shielding constant, and is the magnetic moment of hydrogen nucleus.

From this equation, the resonance frequency decreases according to increasing the shielding effect, and the higher shielding also decreases the binding energy. In the case of a-C:F films with the flow rate ratio $CH_4/CF_4=30/10$ as shown in Fig. 1(a), the C 1s electron orbital spectra by fitting the data with an number of Gaussian peaks consist of two peaks which can be assigned to the C-CF bond and C-F bond. The C 1s electron orbital spectra show the resonance stabilization such as the highest shielding effect due to rich alkyl group and the main peak of binding energy also is lower than any others. On the other hand, the C 1s spectra of a-C:F films with the flow rate ratio $CH_4/CF_4=10/30$ as shown in Fig. 1(c) is broad band from 284 eV to 296.5 eV of four peaks which can be assigned to the C-CF bond, C-F bond, C-F₂ bond and C-F₃ bond. Figure 1(c) shows the effect of the inductive stabilization in a-C:F films due to the interaction between high electronegative atom and C-H hydrogen bond.

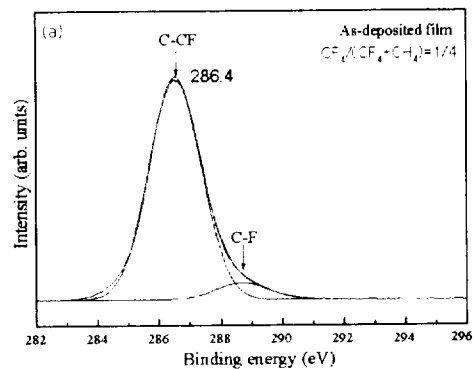


Fig. 1. (a) The C 1s electron orbital spectra of as-deposited film with the flow rate ratio $CF_4/(CF_4+CH_4)=1/4$.

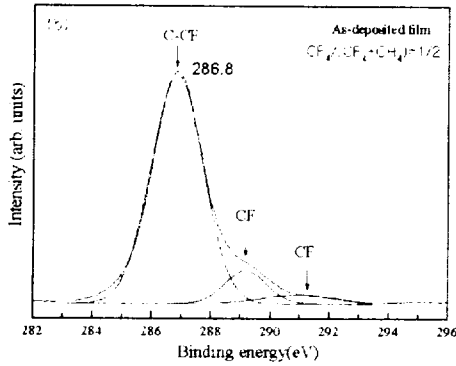


Fig. 1. (b) The C 1s electron orbital spectra of as-deposited film with the flow rate ratio $CF_4/(CF_4+CH_4)=1/2$.

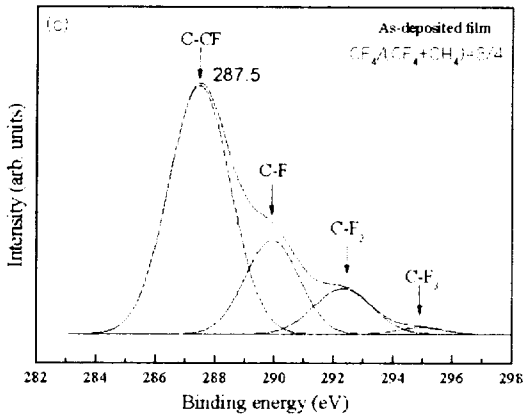


Fig. 1. (c) The C 1s electron orbital spectra of as-deposited film with the flow rate ratio $CF_4/(CF_4+CH_4)=3/4$.

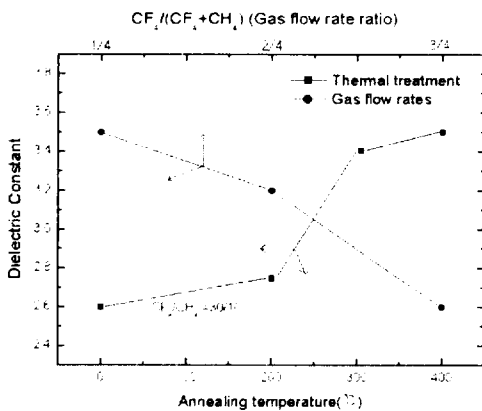


Fig. 2. The dielectric constant of a-C:F films as functions of the flow rate ratio and heat

treatment temperature.

The high electronegative fluorine draws hydrogen at the C-H bond, therefore the bonding structure of a-C:F films becomes strong cross link due to weak bond between C-H atoms. The dielectric constant of a-C:F films with variation of the flow rate ratio is the lowest at the films with the most fluorine flow rate as shown in Fig. 2. Fig. 3(a), (b) and (c) show the C 1s electron orbital spectra of the as-deposited films according to the treatment of various annealing temperature.

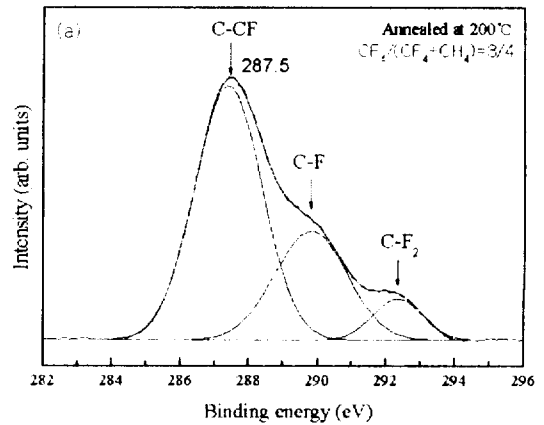


Fig. 3. (a) The C 1s electron orbital spectra of 200 °C annealed film with the flow rate ratio $CF_4/(CF_4+CH_4)=3/4$.

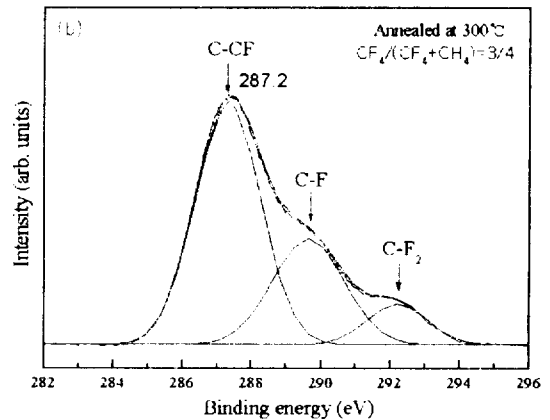


Fig. 3 (b) The C 1s electron orbital spectra of 300 °C annealed film with the flow rate ratio $CF_4/(CF_4+CH_4)=3/4$.

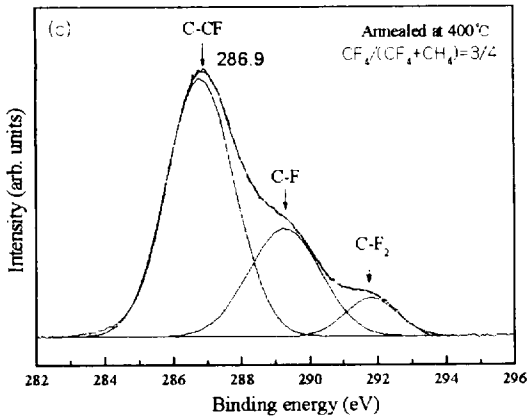


Fig. 3. (c) The C 1s electron orbital spectra of 400 °C annealed film with the flow rate ratio $CF_4/(CF_4+CH_4)=3/4$.

The main peaks of C 1s spectra in annealed films with 200 °C, 300 °C and 400 °C are 287.5 eV, 287.2 eV and 286.9 eV, relatively. The binding energy of C 1s spectra decreases according to increasing the annealing temperature. It means that the bonding strength of the films becomes weak and then, a cross link of the films breaks partly. The bonding structure of annealed films becomes partial cross link. Compare annealed films with as-deposited film, the C 1s spectra of annealed films is narrower than that of as-deposited film. From these results, we know that a-C:F films change from inductive stabilization to the resonance stabilization according to increasing the annealing temperature. The dielectric constant of annealed films as shown in Fig. 2 increases according to increasing the annealing temperature. The cross link bonding structure in a-C:F films is due to the elongation of C-H hydrogen bond by high electronegative fluorine, and decreases the dielectric constant of the films.

IV. CONCLUSION

Fluorinated amorphous carbon films formed various bonding structure due to F and alkyl radicals dissociated according to the flow rate ratio and heating condition. The bonding structure of a-C:F films is described by the resonance and inductive stabilization due to the variation of the electron distribution. The cross link structure due to inductive stabilization is owing to withdrawing of C-H bond by the high electronegative fluorine. The cross link structures improve the mechanical properties such as good adhesion and decrease the dielectric constant of the films.

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