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XPS STUDY ON SN-DOPED DLC FILMS PREPARED BY RF PLASMA-ENHANCED CVD

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ABSTRACT

We synthesized semiconducting Sn-doped diamondlike carbon films by rf plasma-enhanced chemical vapor deposition using an organotin compound as a dopung gas source. XPS quan-titative analysis for the deposited films after 60 s argon ion etching revealed that Sn concen-tration increased with the partial pressure of the organotin compound in the reactant gas. In C 1s spectra, there was a component due to C-Su bond which had a negative chemical shift. C 1s spectra also indicated that the deposited films were relatively sp^2 rich. The chemical shift of the Sn-C bond in Sn $3d_{5/2}$ spectra was about +1.7 eV. The electrical resistivity and the optical transmittance were also investigated.

INTRODUCTION

Diamondlike carbon (DLC) is defined as an amorphous carbon material containing a mixture of sp^3, sp^2 and sp^1 hybridized carbon. DLC films have been prepared by a variety of methods including plasma-enhanced chemical vapor deposition (PECVD), sputtering and ion beam deposition using many types of carbon-bearing solid or gaseous source materials[1]. Because of the superiority of hardness, flatness, low friction and high optical transarency in the infrared region, DLC films have been studied by a lot of researchers in applications to hard coatings, protective laers on magnetic disks and tapes, solid lubricant for dies and antireflective coatings for the infrared optical devieces.

Electrical properties of DLC films, on the other hand, have not been investigated so extensively, since only high electrical resistivity is required for these applications. However, DLC has the possibility of application to acive electronic devices as well as amorphous silicon(a-Si, a-Si:H). The electrical resistivity of DLC is generally very high, so that it is difficult to use undoped DLC films in the active electronic devices. In this study, we prepared semiconduction DLC films by doping Sn atoms using an organotin compound as a doping gas source and investigated their chemical bonding states by X-ray photoelectron spectroscopy(XPS).

EXPERIMENTAL PROCEDURE

We used a parallel-plate rf PECVD system to deposit DLC films. Figure 1 shows the schematic diagram of the deposition system. Vacuun system consisted of a rotary pump and a mechanical booster pump. Reaction chamber and electrode plates were made of

stainless steel. The plate attached upside was grounded and the other was cathode. Subst-ㅌ ㅌㅌrates were set on the former electrode, and the latter had a lot of pinholes through which methane and hydrogen gases, main gas sources, were introduced. Tetramethyltin(Sn $(CH_3)_4$:ㅌTMT) gas was supplied through a gas inlet at the chamber wall. After the reactor was evacuated below 5×10^{-2} Pa, the reactant gases were introduced to a fimal pressure. The partial pressures of methane and hyrogen were controlled by two mass flow conrollers and that of TMT was done by a needle valve. The gas flow rates of both methane and hydrogen were held at 70 ssccm. The partial pressure ratio of TMT *(R P_{TMT}/P_{total})* was varied from 0.08 to 2.4%. We fixed the total pressure, the rf power and the substrate temperature at 50 Pa, 200 W and 473 K. The preparation conditions are summarized in Table Ⅰ.

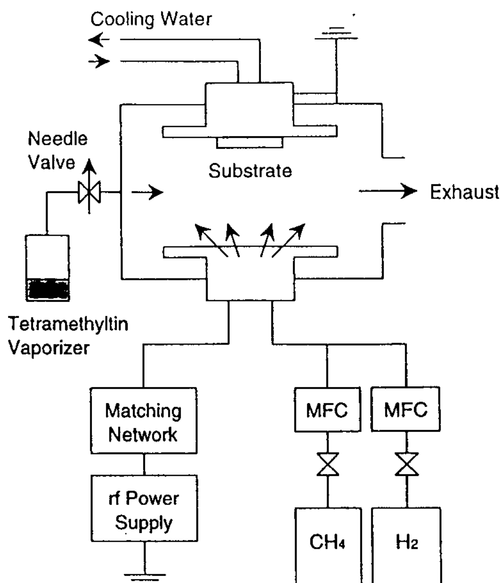

Fig. 1 Schematic diagram of parallel-plate rf PECVD system.

Table Ⅰ Y. Inoue and O. Takai, XPS STUDY ON Sn-DOPED DLC FILMS

Base Pressure	$<5\times10^{-2}$ Pa
Total Pressure	50 Pa
CH_4 Flow Rate	70 sccm
H_2 Flow Rate	70 sccm
Partial Pressure Ratio of Tetramethyltin(R)	0.08~2.4%
Substrate	Si(100)
Substrate Temperature	473K
rf Power	200W
Deposition Time	180min

XPS measurements were carried out using AXIS(Shimadzu-KRATOS) in order to deter-mine the chemical composition and chemical bonding states of the deposited films. XPS working conditions are shown in Table Ⅱ. Since the Sn-doped DLC films were conductive electrically, we could completely prevent the charge-up phenomenon by contacting the sample surfaces to a sample holder using a conducting adhesive tape which was available in a vacuum of $\sim10^{-9}$ Pa. A Gaussian function was used for curve fitting of measured spectra.

Electrical resistivity was measured by van der Pauw method at room temperature. Spectro-scopic measurements in the NUV-NIR region were performed by using a double-beam spectropho-tometer(Shimadzu UV-3101PC).

Table Ⅱ Y. Inoue and O. Takai, XPS STUDY ON Sn-DOPED DLC FILMS

Base Pressure	$<1\times10^{-8}$Pa
X-ray Source	Monochromatic AlKα (1486.6eV)
X-ray Power	120W
Pass Energy	
survey scan	80eV
narrow scan	20eV
Analyzing Area	~3mm×6mm
Resolution	0.6eV
Ar^+ Energy	3keV
Etching Time	60sec
Etching Area	~6mm×10mm

RESULTD AND DISCUSSION

In survey scan measurements (scan-ning region : 0~1300 eV), C, Sn and O were detected for all samples. There were a lot of contaminants such as various types of hydrocarbon, oxygen and water on the film surface because the samples had to be exposed to the air before XPS analyses. Hence we cleaned film surfaces by argon ion bombardment at the energy of 3 keV for 60 s preceding to ech narrow scanning in order to remove the adsorbed species and oxidized layer. The O 1s intensity reduced drastically after this cleaning procedure.

Quantitative Analysis

The concentrations of Sn and C on the cleaed surface were determined from Sn $3d_{5/2}$ and C 1s naroow scan spectra with linear baseline. Sensitivity factors were 4.32 and 0.25 for Sn $3d_{5/2}$ and C 1s, respectively. Figure 2 shows the dependence of the concentration ratio of Sn to C on the TMT partial pressure ratio. The Sn/C ratio increases monotonically with R. Sn atoms are effectively included in the DLC films prepared by rf-PECVD with very low prtial pressure of TMT

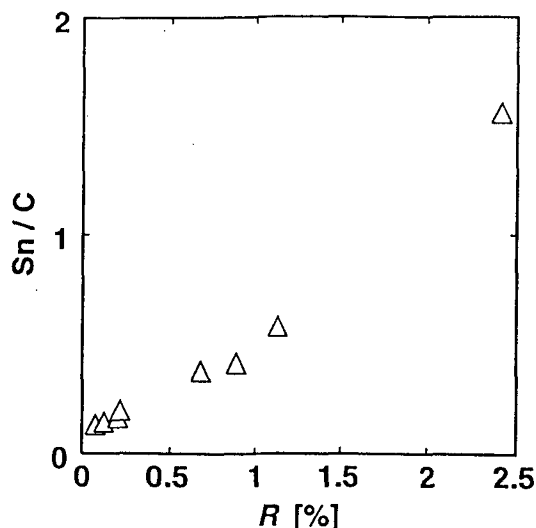

Fig. 2 Dependence of the concentration ratio of Su to C (Su/C) on the TMT partial partial pressure ratio R.

XPS C 1s

Figure 3 shows XPS C 1s spectrum of the Sn-doped DLC film prepared at R=0.2%. It has a peak around at 285 eV and a shoulder at lower binding energy. This spectrum is fitted with two Gaussian components in the energy region lower than 286 eV. The peak positions of components 1 and 2 are 283.2 eV and 284.8 eV. It has been reported that C 1s spectra for carbided show negative chemical shifts[2-6]. For example, C 1s binding energy for a SiC thin film formed on Si(100) with a well-collimated C_2H_2 beam was 283.3 eV[2]. The chemical shift effect is simply illustrated by the charge potential model[7]. Since the electronegativity of silicon is 1.8 and that of carbon 2.5, the carbon atom localizes the electrons concerning to Si-C bonds. Therefore

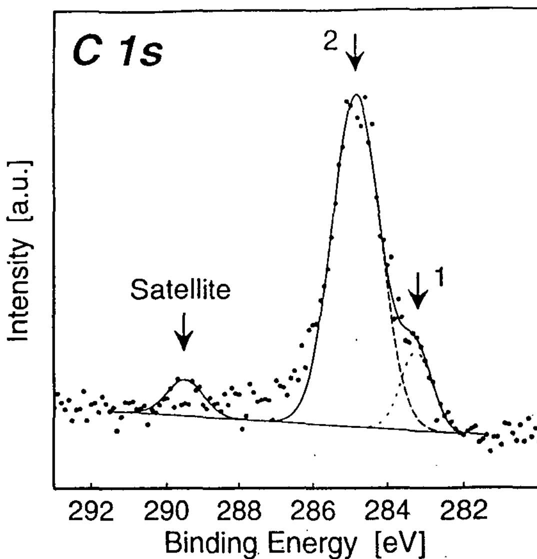

Fig. 3 XPS C is spectrum for Sn-doped DLC film prepared at R=0.2%. Dots are experimental data and lines are fitted. The film surface was cleaned by Ar^+ etching for 60 s.

the C 1s bnding energy shows negative chemical shift. The C 1s chemical shift for Sn-C bond is estimated to be same as that for silicon carbide since the electronegativity of tin equals to that of silicon. The binding energy of component 1 in Fig. 3 is very close to that of SiC. Therefore we conclude that these carbon atoms are directly bonded with Sn atoms. This study is the first report on XPS chemical shift of Sn-C bond for a solid state material including Sn and C.

Component 2 represents C-C or C-H bonds. Jackson et al. reported that the C 1s envelope for sputtered amorphous carbon films was a convolution of three peaks which were assignable to sp^2 hybridized carbon, sp^2 hybridized carbon and an sp^2 satellite peak, possibly due to π-π^* transition[8]. In this study, we do not deconvolute the C 1s spectrum to sp^2 and sp^3 peaks because these components are not separated apparently. The spectrum in Fig. 3, however, has a small peak around at 289.5 eV, which is supposed to be a shake-up satellite due to π-π^* transition. A long tail up to 289 eV also indicates the existence of π bonds[9]. Therefore the films prepared are relatively sp^2-rich DLC.

XPS Sn $3d_{5/2}$

The bonding states of Sn atoms were analyzed from the XPS Sn $3d_{5/2}$ spectrum. Figure 4 shows the Sn $3d_{5/2}$ spectrum after 60 s Ar^+ bombardment for the Sn-doped DLC film prepared at R=0.2%. We used two Gaussian components to fit the experimental data. The binding energy of component 1 is 484.6 eV, which exactly corresponds to that of metallic tin[10, 11]. This component is due to the reduction process induced by the aron ion bombardment. This is shown clearly in Fig. 5 which indicates the dependence of the lineshape of the Sn $3d_{5/2}$ spectrum on the etching

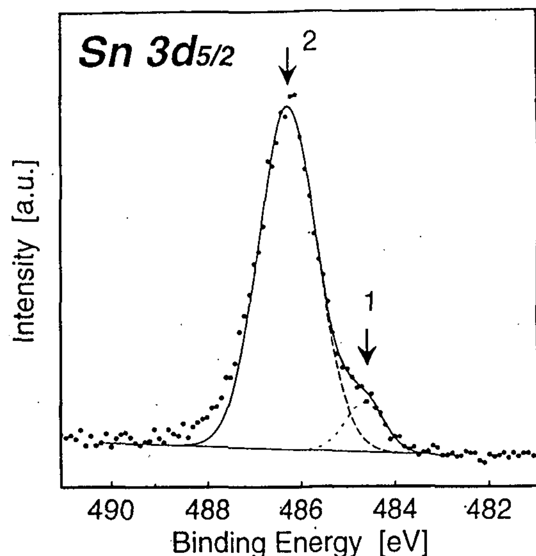

Fig. 4 XPS Sn $3d_{5/2}$ spectrum for the Sn-doped DLC film prepared at R=0.2%. Dots are experimental data and lines are fitted. The film surface was cleaned by Ar^+ etching for 60 s.

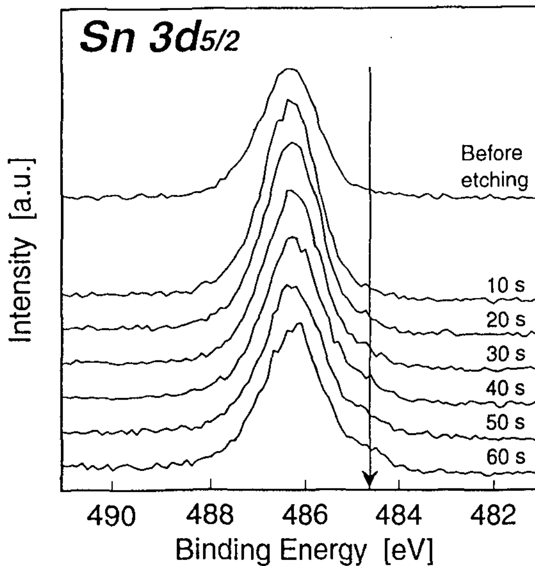

Fig. 5 XPS Sn $3d_{5/2}$ spectrum for the Sn-doped DLC film prepared at R=0.2%. as afunction of Ar^{+}sputtering time. The arrow drawn at 484.6 eV indicates the binding energy for the metallic Sn.

time. There is no shoulder in the spectrum measured before cleaning and the shoulder around at 485 eV becomes obvious as the argon ion etching proceeds.

Component 2 represents Sn-C bonds. The binding energy of this component is 486.3 eV and the chemical shift from the bonding state of metallic tin is+1.7 eV, which is lower than that for SnO_2(+2.2eV)[10,11]. We have reported the chemical bonding states of tin-nitride films prepared by reactive sputtering[11]. The chemical shift for tin-nitride films is+ 1.5 eV. Because the electronegativity of carbon is lower than both hitrigen and oxygen, the chemical shift of Sn-C bond cannot be explained only by electronegativity. It is needed to consider the coordinate number of tin atom and the bond length of Sn-C. There is a small tail in the higher binding energy region. The Sn $3d_{5/2}$ spectra for metallic tin, tin dioxide and tin nitride also have same tails and the origin is not clear at present.

Physical Properties

All Sn-doped DLC films synthesized in this sudy showed p-type semiconductivity. The electrical resistivity decreased drastically by doping Sn and the measured value was in the order of 10^{-2}~10^{-3}Ωcm. Optical trnsmittance was reduced especially in the infrared region. These ws a tendency that both the resistivity and the transmittance reduce with the increase in Sn/C concentration ratio.

CONCLUSIONS

Sn-doped DLC films were synthesized by rf-PECVD method using tetra-methyltin as a doping gas, and their chemical bonding states were investigated by XPS. Tin atoms were effectively included in the deposited films. In the XPS C 1s spectrum, there was a component shifted to 283.2 eV. This component indicates clearly the existence of Sn-C bonds. A small peak at 289.5 eV and a long tail of the C 1s main peak represent the sp^2-rich character of the deposited film. In this study we made clear that the semiconductive DLC films with low electrical resistivity can be synthesized using an organometallic compound as a doping gas. This suggests that metal-doped DLC has the possibility of application to active electronic devices. The dependence of the electrical properties on the dopant element should be studied in the future.

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