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# The Mechanical and Optical Properties of Diamond-like Carbon Films on Buffer-Layered Zinc Sulfide Substrates

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Diamond-like carbon(DLC) films were deposited on buffer-layered ZnS substrates by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) method. Ge and GeC buffer layers were used between DLC and ZnS substrates to promote the adhesion of DLC on ZnS substrates Ge buffer layers were sputter deposited by RF magnetron sputtering and GeC' buffer layers were deposited by same method except using acetylene reactive gas. The relationship between film properties and depositon conditions was investigated using gas pressure, RF power and dc bias voltage as PECVD parameters The hardness of DLC films were measured by micro Vickers hardness test and the adhesion of DLC films on buffer-layered ZnS substrates were studied by Sebastian V stud pull tester. The optical properties of DLC films on buffer-layered ZnS substrates were characterized by ellipsometer and FTIR spectroscopy.

***Key words :*** Diamond-like Carbon(DLC), Ge, GeC, Buffer Layers, ZnS, IR, PECVD

## I. Introduction

Diamond-like carbon(DLC) film is expected as hard protective coating material for mechanical and optical purposes. Because DLC has good mechanicl and optical properties such as high hardness(3000~9000 kg/mm$^2$) and high transparency from visible to IR region. it can be used to protect weak IR materials, such as zinc sulfide(ZnS).[1] However the adhesion of DLC on ZnS is poor in general. To serve as a protective film, the adhesive force between DLC and ZnS must be large enough to withstand the high internal stress of DLC films, which cause film delaminationa. We deposited Ge and GeC as buffer alyers between DLC and ZnS by RF sputtering to promote adhesion of DLC on ZnS and to ensure excellent optical performance. DLC, as a hard protertive layer, was deposited on Si and buffer-layered ZnS substrate by PECVD. The properties of Ge, GeC buffer layers and DLC were charactirized by X-ray diffraction, FT-IR, Ellipsometer, Sebastian V stud-pull test, Raman spectrum and dynamic load hardness test.

## II. Experimental Procedure

### *1. Ge buffer layer deposition*

Ge films were deposited on ZnS substrate by RF sputtering method. We have fixed Ar flow rates as 20 SCCM and target-substrate distance as 10 cm. We have varied the process conditions to find the variationof film properties. Pressure(1, 5, 10, 20, 50 mtorr), RF power(50, 100, 150 W), time(2, 5, 10, 15, 20 min) and substrate temperature(no heating, 200, 250, 300, 350°C) were varied. The basic condition was 10 mtorr, 150 W, 5 min and no substrate heating. Ge target was pre-cleaned by Ar sputtering for 5 min.

### *2. GeC buffer layer deposition*

We used a Ge target, Ar gas and $C_2H_2$ gas as reactive sputtering sources. Ge target was Ar plasma cleaned before $C_2H_2$ was introduced. The deposition variables for GeC reactive sputtering were pressure(1, 5, 10, 20, 50 mtorr), RF power(50, 100, 150, 200, 250 W), time(2, 5, 10, 15, 20 min), substrate temperature(no heating, 200, 250, 300, 350°C) and the ratio of $C_2H_2$ gas to Ar gas(1/5, 1/3, 1/2, 1/1, 2/1). The basic common condition is 10 mtorr, 150 W, 5 min, no heating of substrate and $C_2H_2$ to Ar ratio, 1/2. In each process the basic condition was fixed except on variable.

### *3. DLC film deposition*

We have deposited DLC films on Si substrates by PECVD, whose process parameters were pressure(1, 5, 10, 20, 50 mtorr), RF power(50, 100, 150, 200, 250 W), time(5, 10, 20, 30, 60 min), substrate dc self-bias voltage(-300, -400, -500, -600, -700V), $C_2H_2$/Ar ratio(1/5, 1/2, 1/1, 2/1, 5/1) and $C_2H_2/H_2$ ratio(1/5, 1/2, 1/1, 2/1, 5/1). The basic common conditions were 10 mtorr, 100 W, 10 min, $C_2H_2$ flow rate 20 SCCM. The base pressure of DLC coating was below $10^{-4}$ mtorr and the substrates were Ar sputter-cleaned for 1 min at 10 mtorr and 150 W before deposition.

### 4. Film characterization

The film structure of Ge and GeC was investigated by X-ray diffraction. Film thickness was measured by α-step and refractive index by ellipsometer at 1290 nm. Vickers hardness of DLC was obtained from dynamic ultra micor hardness test(Shimadzu DUH-202). Adhesion of films on ZnS substrates was observed by stud-pull test using Sebastian V tester. IR transmittance of Ge, GeC and DLC film was measured by FTIR. Through Raman spectrometer film materials were identified.

## III. Results

### 1. Ge films

Table 1. shows the variations of film thicknesses, refractive indices and IR transmittances according to the deposition parameters. The thicknesses of Ge measured by α-step was used as a guide to determine the film refractive index and thickness with an ellipsometer. The refractive index of Ge is 4.1 and its melting point is 1210 K. In this table the refractive index of Ge is not always the original value of about 4.1, which indicates that the film is porous at the deposition conditions. The value of FTIR transmittance at 10 μm is obtained by extracting the effect of zinc sulfide substrate. The right end column shows the values normalized to the film thickness of 1000 Å using the following equation.

$$I = I_0 exp(-\alpha x) \qquad (1)$$

I=Intensity of the ray passed the film
$I_0$=Intensity of the incident ray
α=Absorption coeficient of the film
x=Film thickness

To find out the crystal structure of the film deposited by RF sputtering from Ge target, we used the X-ary diffraction method. Fig. 1(a) is the X-ray diffraction pattern of Ge on ZnS substrate which was heated at 350°C during deposition (Table 1. No.S-16). There are high ZnS peaks along with very low peaks. Fig. 1(b) is the magnified picture of Fig. 1(a). Because the film thickness is

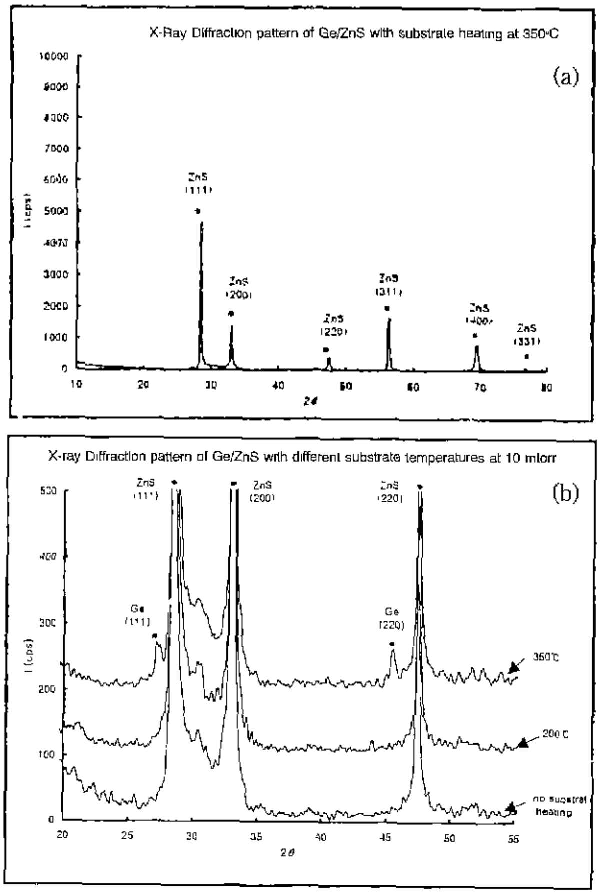


**Fig. 1.** (a) X-ray diffraction pattern of Ge/ZnS with substrate heating at 350°C and (b) X-ray diffraction pattern of Ge/ZnS with change of substrate heating temperature.

**Table 1.** Ge Film Properties According to the Deposition Conditions

| No. | Condition | Film | Substrate | α-STEP (Å) | Ellipsometer (Å) | Ellipsometer (n) | FTIR (%) at 10 μm | FTIR (%) Normal |
|---|---|---|---|---|---|---|---|---|
| S-1 | 1 mtorr | Ge | ZnS | 1535 | 2063 | 2.3256 | 88.2 | 94.1 |
| S-2 | 5 mtorr | Ge | ZnS | 1715 | 1713 | 3.3416 | 91.7 | 95.1 |
| S-3 | 10 mtorr | Ge | ZnS | 1500 | 1622 | 2 9058 | 97.3 | 98.3 |
| S-4 | 20 mtorr | Ge | ZnS | 1658 | 1629 | 2.3707 | 98.2 | 98.9 |
| S-5 | 50 mtorr | Ge | ZnS | 840 | 767 | 2.4096 | 97.6 | 96.9 |
| S-6 | 50 W | Ge | ZnS | | 1622 | 2.1722 | 99.0 | 99.4 |
| S-7 | 100 W | Ge | ZnS | | 1203 | 2.5759 | 97 8 | 98.2 |
| S-8 | 200 W | Ge | ZnS | 2850 | 1306 | 2.2115 | 93.3 | 94.8 |
| S-9 | 2 min | Ge | ZnS | 719 | 776 | 2.8031 | 99.3 | 99.1 |
| S-10 | 10 min | Ge | ZnS | 3091 | 3438 | 4.0407 | 94.9 | 98.5 |
| S-11 | 15 min | Ge | ZnS | 5236 | 4919 | 2.2787 | 84.9 | 96.7 |
| S-12 | 20 min | Ge | ZnS | 6364 | 6633 | 2.7351 | 90.4 | 98.5 |
| S-13 | 200°C | Ge | ZnS | 1250 | 1389 | 4.1871 | 95.1 | 96.4 |
| S-14 | 250°C | Ge | ZnS | 1250 | 1667 | 7.5207 | 91.5 | 94.8 |
| S-15 | 300°C | Ge | ZnS | 1100 | 1287 | 9.9198 | 90.4 | 92.5 |
| S-16 | 350°C | Ge | ZnS | 1200 | 1279 | 4.2714 | 93.4 | 94.8 |

1279 Å and the intensity of Ge peak is weak compared to ZnS peaks, Ge film peak was difficult to detect clearly. Still, we could find Ge peaks as the substrate temperature was increased, which means that Ge thin films were crystallized by substrate heating.

Fig. 2 is the Raman spectrum of S-16. The thin curve is Raman spectrum of Ge bulk sample and the thick one is Ge/ZnS sample(S-16). Both curve have the same peak at same wave number 308 $cm^{-1}$. From the X-ray diffraction and Raman spectrum we could confirm that the Ge film deposited at 350°C has crystalline phase.

Fig. 3 shows the result of stud pull test of Ge/ZnS sample. The thickness of germanium film was 604 Å and the deposition was done at 2 min, 150 W, 20 mtorr and 200°C. As indicated in this photograph the Ge film displayed a very good adhesion to the ZnS substrate. The adhesive force between Ge film and ZnS substrate is higher than the cohesion of the ZnS, as evidencec by the fracture in the substrate. In the stud surface the pulled-

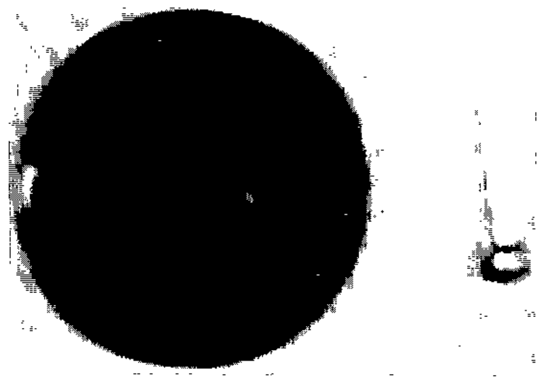

**Fig. 3.** The result of stud pull test of Ge/ZnS sample.

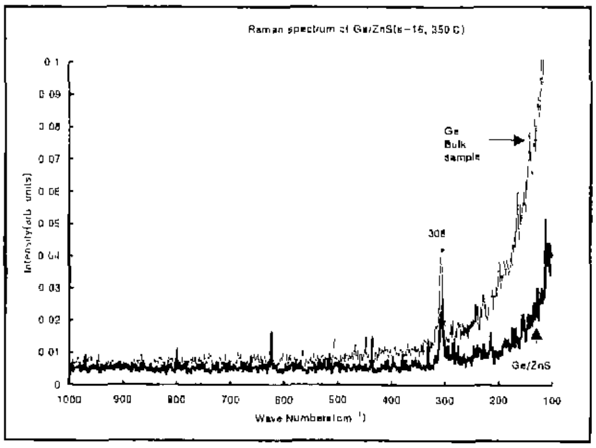


**Fig. 2.** Raman spectrum of Ge/ZnS(S-16, 350°C).

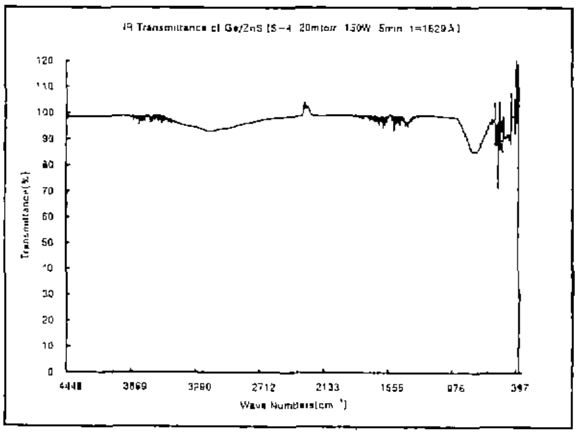

**Fig. 4.** The IR transmittance of Ge/ZnS(S-4, 20 mtorr, 150 W, 5 min. t=1629 Å).

**Table 2.** GeC Film Properties According to the Deposition Conditions

| No. | condition | Film | Substrate | α-STEP (Å) | Ellipsometer (Å) | Ellipsometer (n) | FTIR (%) at 10 μm | FTIR (%) Normal |
|---|---|---|---|---|---|---|---|---|
| S-29 | 1 mtorr | GeC | ZnS | 1229 | 1162 | 1.6856 | 100.5 | 100.4 |
| S-30 | 5 mtorr | GeC | ZnS | 1452 | 1545 | 1.6634 | 99.6 | 99.8 |
| S-31 | 10 mtorr | GeC | ZnS | 1378 | 1338 | 1.6603 | 100.8 | 100.6 |
| S-32 | 20 mtorr | GeC | ZnS | 1170 | 1436 | 1.6589 | 97.4 | 98.2 |
| S-33 | 50 mtorr | GeC | ZnS | 1499 | 1592 | 1.6037 | 101.3 | 100.8 |
| S-34 | 50 W | GeC | ZnS | 601 | 714 | 1.6096 | 101.4 | 102.0 |
| S-35 | 100 W | GeC | ZnS | 1170 | 1118 | 1.6430 | 100.3 | 100.3 |
| S-36 | $C_2H_2$ : Ar=1 : 5 | GeC | ZnS | 1331 | 1224 | 1.6574 | 101.3 | 101.1 |
| S-37 | $C_2H_2$ : Ar=1 : 3 | GeC | ZnS | 1113 | 1234 | 1.6618 | 99.5 | 99.6 |
| S-38 | $C_2H_2$ : Ar=1 : 1 | GeC | ZnS | 1771 | 1889 | 1.7077 | 101.5 | 100.8 |
| S-40 | 200°C | GeC | ZnS | 1083 | 1002 | 1.6151 | 100.2 | 100.2 |
| S-41 | 250°C | GeC | ZnS | | | | 101.2 | |
| S-42 | 300°C | GeC | ZnS | | 683 | 1 5827 | 100.9 | 101.3 |
| S-43 | 350°C | GeC | ZnS | | | | 101.2 | |
| S-44 | 2 min | GeC | ZnS | 602 | | | 100.4 | |
| S-45 | 10 min | GeC | ZnS | 2539 | | | 100.4 | |
| S-46 | 15 min | GeC | ZnS | 4047 | | | 100.9 | |
| S-47 | 20 min | GeC | ZnS | 4841 | | | 99.8 | |

off ZnS piece stuck together with Ge film. In this test the adhesion value measured by the Sebastian V tester was 195.1 kg/cm$^2$.

Fig. 4 shows the IR transmittance curve of Ge film deposited by sputtering at 20 mtorr, 5 min and 150 W. The thickness of Ge film was 1629 Å. This transmittance value was obtained by extracting the effect of ZnS substrate

Table 2 shows the refractive indices and IR transmittance of GeC deposited by reactive sputtering using Ar and $C_2H_2$ gas. The FTIR transmittance of GeC which was obtained extracting the effect of ZnS was excellent. In other papers the refractive Index of GeC was found to be in the range of 2 to 4 depending on the deposition process.[2] In our experiment we have obtained the GeC refractive index values in 1.6 to 1.7 range. In our results the refractive index of GeC decreased as the reactive sputtering pressures increased. Also the increase of $C_2H_2$ to Ar ratio increased refractive index.

Fig. 5 shows the XRD pattern of GeC film that was deposited by reactive sputtering with substrate heating at 350°C(S-43). We could not find clean GeC peaks.

Fig. 6 is Raman spectra of ZnS substrate and GeC film

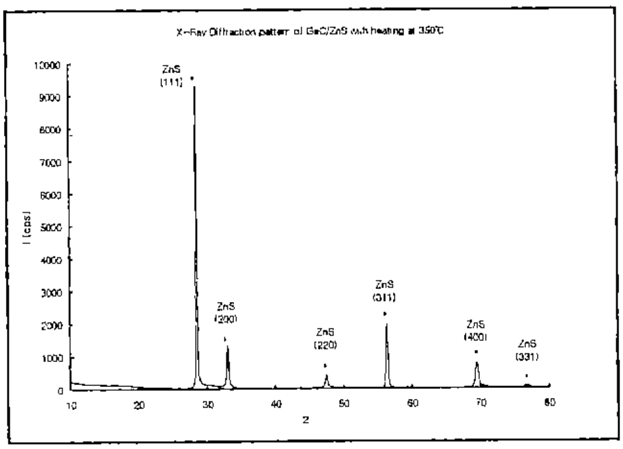


**Fig. 5.** X-ray diffraction pattern of GeC/ZnS with substrate heating of 350°C.

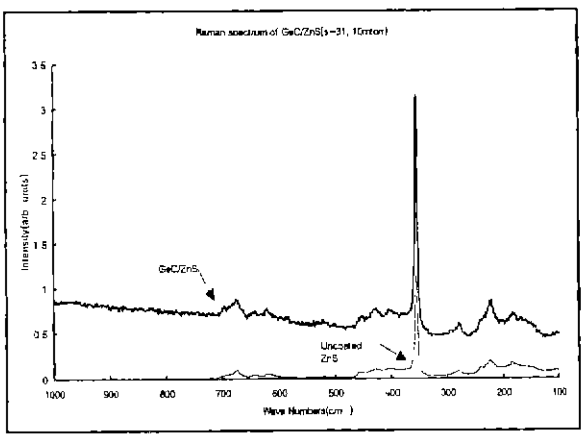


**Fig. 6.** Raman spectrum of GeC/ZeS(S-31, 10 metorr).

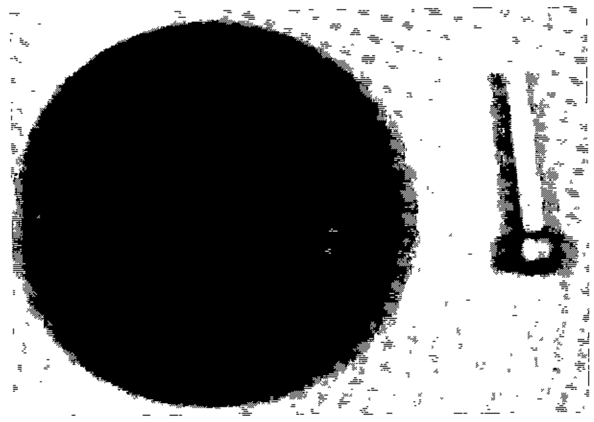

**Fig. 7.** The result of stud pull test of GeC/ZnS sample.

deposited on ZnS substrate. The two curve seems to be identical and there seems to be no unique crystalline phase peak of GeC film. From the result of X-ray diffraction and Raman spectra, we can conclude that this GeC film has amorphous phase.

Fig. 7 is the result of GeC film adhesion test using Sebastian V. The deposition condition for this sample was 2 min, 150 W, 10 mtorr and $C_2H_2$ : Ar=1 : 2. As indicated in this figure, the GeC film displayed a very good adhesion

**Table. 3.** DLC Film Deposition Results (substrate : Si)

| No. | condition | α-STEP (Å) | Ellipsometer (Å) | Ellipsometer (n) |
|---|---|---|---|---|
| S-56 | 1 mtorr | 546 | 675 | 2.2283 |
| S-57 | 5 mtorr | 1443 | 1591 | 2.2735 |
| S-58 | 10 mtorr | 2776 | 3803 | 3.1020 |
| S-56 | 20 mtorr | 4756 | 4752 | 2.3189 |
| S-60 | 50 mtorr | 11360 | 11040 | 2.2296 |
| S-61 | 50 W | 1579 | 1735 | 2.2237 |
| S-62 | 100 W | 3021 | 2800 | 3.2977 |
| S-63 | 150 W | 4137 | 4199 | 2.3309 |
| S-64 | 200 W | 5294 | 6443 | 2.8255 |
| S-65 | 250 W | 7102 | 6314 | 2.6620 |
| S-66 | -300 V | 1969 | 1836 | 2.2493 |
| S-68 | -400 V | 2688 | 1827 | 2.9239 |
| S-69 | -500 V | 3287 | 3421 | 2.3718 |
| S-70 | -600 V | 4370 | 4323 | 2.3703 |
| S-71 | -700 V | 4925 | 4281 | 2.6513 |
| S-72 | 5 min | 1358 | 1372 | 2.2343 |
| S-73 | 20 min | 6111 | 7116 | 3.1462 |
| S-74 | 30 min | 8167 | 8459 | 2.9763 |
| S-75 | 60 min | 19097 | 18074 | 2.4745 |
| S-76 | $C_2H_2$:Ar=1:5 | 1647 | 1616 | 2.3998 |
| S-77 | $C_2H_2$:Ar=1:2 | 2608 | 1682 | 2.9590 |
| S-78 | $C_2H_2$:Ar=1:1 | 3495 | 3016 | 2.6902 |
| S-79 | $C_2H_2$:Ar=2:1 | 2361 | 2053 | 2.7277 |
| S-80 | $C_2H_2$:Ar=5:1 | 2899 | 2987 | 3.2503 |
| S-82 | $C_2H_2$:$H_2$=1:5 | 879 | 857 | 1.8696 |
| S-83 | $C_2H_2$·$H_2$=1:2 | 1003 | 1313 | 2.1753 |
| S-84 | $C_2H_2$:$H_2$=1.1 | 1806 | 1825 | 2.2475 |
| S-85 | $C_2H_2$:$H_2$=2.1 | 1829 | 1873 | 2.2698 |
| S-86 | $C_2H_2$:$H_2$=5:1 | 2472 | 2264 | 2.4898 |

to the ZnS substrate. The adhesive force between the GeC film and the ZnS substrate is higger than the cohesion of ZnS, as evidenced by the occurrence of fracture in the ZnS substrate. In this test the fracture force in ZnS substrate was 240 kg/cm$^2$.

Table 3. shows the result of DLC film deposition by PECVD. When the $H_2/C_2H_2$ ratio was increased, the refractive index of DLC decreased.

Fig. 8 shows the Raman spectrum of 1.8 μm thick DLC film deposited for 60 minutes.

To check the adhesions of DLC films on various buffer layered ZnS substrates, we have made samples of DLC/Ge/ZnS, DLC/GeC/ZnS and DLC/GeC/Ge/ZnS. Ge and GeC buffer layers were deposited with substrate heating at 200°C. The thickness of DLC film was 3500 Å. As it was witnessed in Fig. 9, 10 and 11, they all showed very good adhesion to ZnS substrate. In all three cases the fracture occurred in the ZnS substrate, which indicates excellent adhesion between DLC and Ge and GeC buffer layers the depth which the indenter displaced during loading. At the maximum load the indenter stops for 5 seconds. After 5 second unloading time, the displacement recovered as much of elastic de-

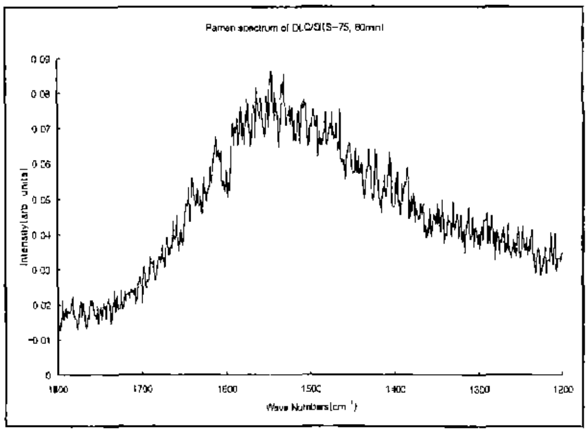


**Fig. 8.** Raman spectrum of DLC/Si (S-75,60 min).

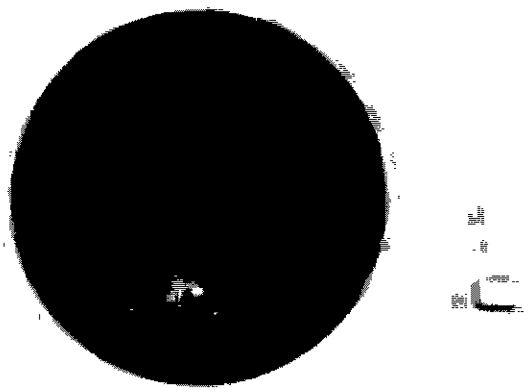

**Fig. 9.** The result of stud pull test of DLC/Ge/ZnS sample (fracture force : 39.1 kg/cm$^2$)

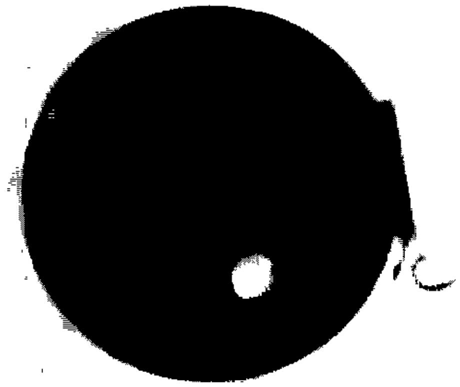

**Fig. 10.** The result of stud pull test of DLC/GeC/ZnS sample (fracture force : 37.7 kg/cm$^2$).

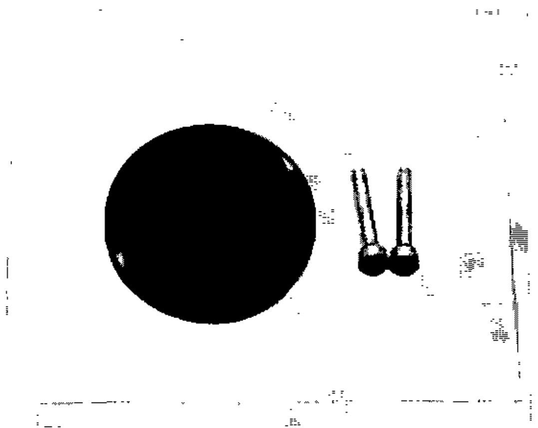

**Fig. 11.** The result of stud pull test of DLC/GeC/Ge/ZnS sample.

formation. D2 is the length of displacement not recovered. From this value the computer calculates the Vickers Hardness of films. That was found to have 6389 kg/mm$^2$ Vickers hardness.

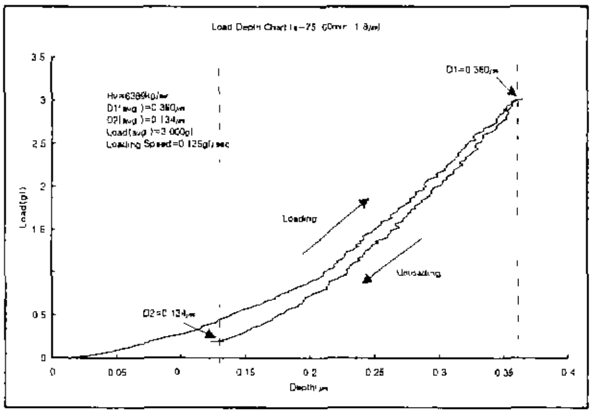


**Fig. 12.** The dynamic ultra micro hardness test result.

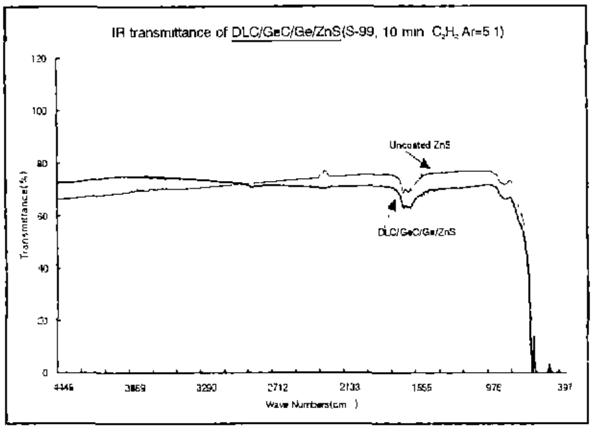


**Fig. 13.** The IR transmittance of DLC/GeC/Ge/ZnS system.

To find out the mechanical hardness of DLC film, we used the *Dynamic Ultra Micro Hardness Tester* at 3.00 gf load and 0.135 gf/sec loading speed. Fig. 12 shows the load depth chart of our 1.8 μm-thick DLC film. In a load depth chart, D1 shows the depth which the indenter displaced during loading. At the maximum load the indenter stops for 5 seconds. After 5 second unloading time, the displacement recovered as much of elastic deformation. D2 is the length of displacement not recovered. From this value the computer calculates the Vickers Hardness of films. that was found to have 6389 $kg/mm^2$ Vickers hardness.

Fig. 13 shows the IR transmittance of a DLC (3500 Å)/Ge(650 Å)/Ge(600 Å)/ZnS sample. Thin line curve represents the IR transmittance of uncoated ZnS substrate. The thick curve, the IR transmittance of DLC on GeC/Ge/ZnS substrate, is very close to the transmittance of uncoated ZnS substrate.

## IV. Summary

We could deposit high hardness DLC film that has excellent adhesion on Ge and GeC buffer layered ZnS substrate. The main summaries are as follows :

1) Sputter coated Ge and GeC buffer layers show excellent IR transmittance. When they were deposited at 200°C or highter, their adhesive forces on ZnS substrate are higher than the cohesion of ZnS

2) The adhesion force of DLC films on the Ge and GeC buffer layers is strong enought that the fracture occured in ZnS during the adhesion test.

3) The hardness of DLC film deposited by PECVD using $C_2H_2$ as a source gas is as high as 6389 $kg/mm^2$, which is enought to be used as a wear resistant protective coating on ZnS

4) The FTIR results show that the DLC/GeC/Ge/ZnS system has transmittance spectrum very close to that of bare ZnS substrate.

5) DLC/Ge and DLC/GeC coatings are hard and strongly adherent to ZnS and have high IR transmittance. Therefore, they can be used successfully as wear resistant protective coatings on ZnS.

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