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Effect of film thickness and interlayer on the adhesion strength of diamond like carbon films on different substrates

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Abstract

The addition of an interlayer is often used to increase the adhesion strength in thin film coating. For diamond like carbon (DLC) films, titanium and chromium are two common interlayer materials to enhance adhesion, especially for metal substrates. In an attempt to explore interlayer effect on nonmetal substrates, plasma enhanced chemical vapor deposition (PECVD) was utilized to deposit DLC with methane on silicon and glass substrates with interlayer titanium and chromium. The film structure and adhesion strength were studied by Raman spectroscopy, optical microscope, nanoindentation and nanoscratch.

For DLC on silicon substrates without interlayer, the results show as the film thickness increases, the ratio of I(D)/I(G) increases and the hardness decreases. For DLC on silicon substrate with interlayer, both interlayers do not enhance the adhesion strength. For glass substrate, the chromium showed improved adhesion strength only in small film thickness (200 nm). As the film thickness increases, the peeling of the DLC thin film deteriorated for both interlayers.

These phenomena were examined by the bonding structure, hardness, nanoscratch and residual stress. As the film thickness increases, the I(D)/I(G) ratio increases and the fraction of sp^3 decreases. This indicates as the film thickness increases, the bonding is towards graphite structure and reducing hardness. The high sp^2 fraction and low hardness explain the poor adhesion of large film thickness. The reasons for chromium acting as a better interlayer on glass than on silicon are attributed to the low residual stress and preferable carbide formation. The similarity in the magnitude of coefficient of thermal expansion between chromium and glass results in less residual stress. Another possibility is the carbide formation on chromium interface which should enhance the adhesion. This hypothesis is currently under investigation.

Keywords: Interlayer; Adhesion; Residual stress

1. Introduction

Diamond like carbon film has many potential applications like optics, micro-electronics, tooling, and the automobile industry due to their high hardness, low friction coefficient, anti-corrosion and excellent biocompatibility. Many factors limit the performance of DLC, poor adhesion due to high compressive stress being the most critical one. There are many methods to improve the adhesion in DLC, for example, metal-containing DLC (Me-C:H) by sputtering [1,2], whisker composite [3], DLC–Si coating [4], and deposition of interlayers like Si, Ti, Cr, or W [5,6]. While adding an element is simpler than depositing another layer, there are applications where an interlayer is necessary. One example is the use of DLC as the passivation in the SAW filter with Al electrode on $LiTaO_3$ substrate [7]. In this case, the Al electrode is sandwiched between DLC and $LiTaO_3$ and its role is like an interlayer. Previous studies on interlayer effect focus primarily on metallic substrates and the associated tribological properties [8–11]. There has been very little work on nonmetal substrates such as silicon and glass. It is well known that these two substrates are primary materials in miniaturization technology. For successful DLC application in miniaturization technology, it is necessary to understand the performance of DLC on these substrates. In the present study, this issue has been addressed by evaluation on DLC adhesion over different interlayer/substrate combinations.

2. Experimental procedure

Silicon (p-type (100) 4″ wafer) and glass (Corning 1737) were used as the substrates for DLC deposition. Two interlayers

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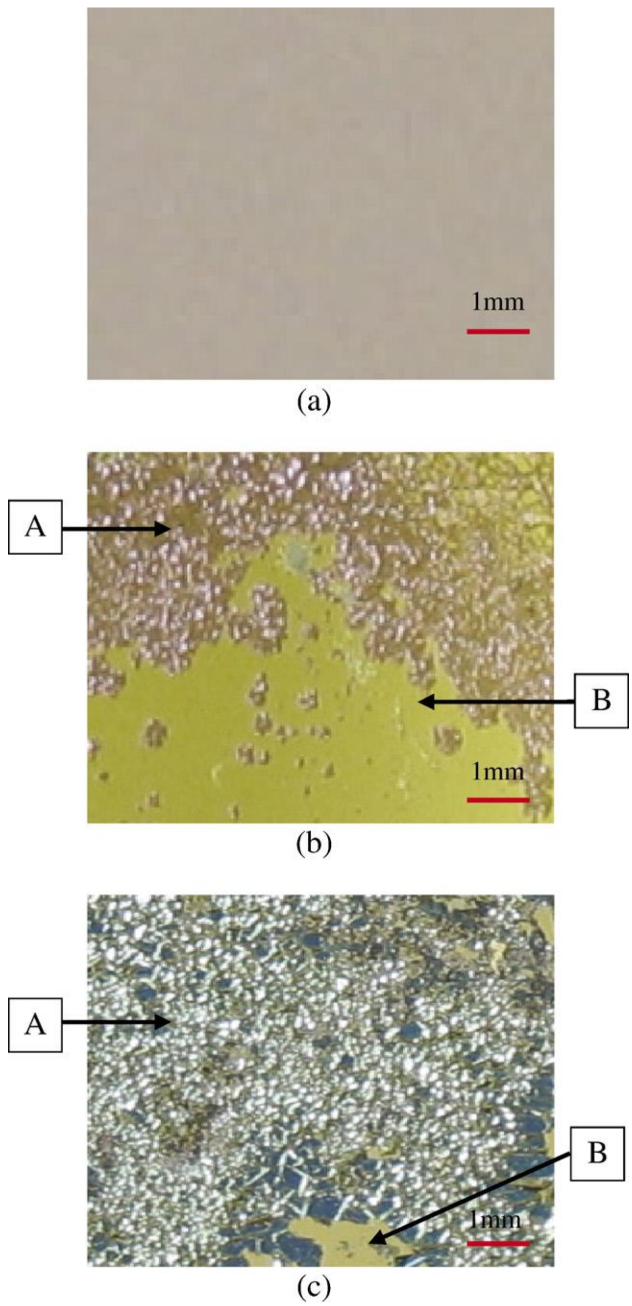

Fig. 1. The micrographs of 200 nm DLC with 40 nm interlayer (a) DLC/Si, (b) DLC/Cr/Si, and (c) DLC/Ti/Si. The arrow A indicates the peeling region and arrow B indicates the good adhesion region.

chromium and titanium were utilized to enhance the adhesion. Chromium was deposited by sputtering at 10^{-3} Torr base pressure with argon flow rate 20 sccm. Titanium was deposited by E-beam evaporation at 4×10^{-3} Torr base pressure. The film thickness of chromium and titanium was controlled by deposition time and the interlayer film thickness was measured at about 40 nm. The DLC film was grown by r.f. plasma chemical vapor deposition (CVD) with methane at base pressure 10^{-3} Torr and at substrate temperature 200 °C. The flow rate of methane is 20 sccm and the bias is at 300 V. The film thickness is controlled by the deposition time. Before each deposition, the substrates were ultrasonically cleaned for 20 min in acetone, blown dry and placed in deposition chamber. After deposition, the film thickness was measured by surface profiler (Alpha-Step 500, KLA-Tencor). The structure of the DLC films was analyzed by Raman spectroscopy (Renishaw, wave length 514.5 nm). The hardness modulus was measured by nanoindentation test (Nanoindenter XP, MTS) using Berkovich indenter. For thicker films, the adhesion strength was assessed with optical microscope (Nikon L150) by qualitatively comparing the peeling degree in each sample. For thinner films with good adhesion, the adhesion was measured by nanoscratch test (NanoTest, Micromaterials) with diamond indenter on the face direction to delaminate the film via linearly increasing load. The

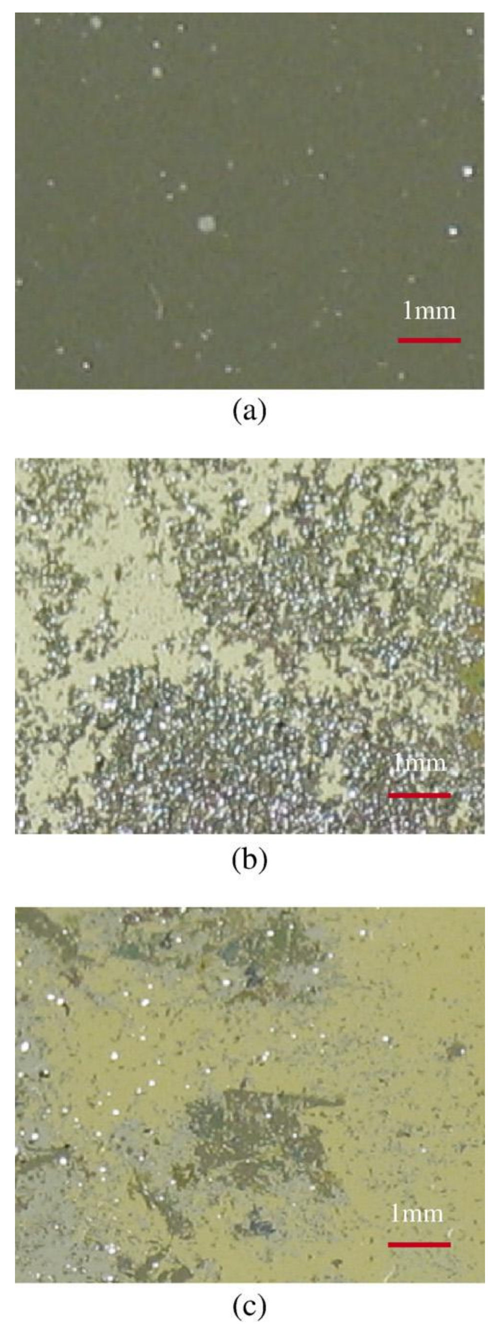

Fig. 2. The micrographs of 870 nm DLC with 40 nm interlayer (a) DLC/Si, (b) DLC/Cr/Si, and (c) DLC/Ti/Si.

Table 1
Raman spectra of DLC film on silicon substrate (without interlayer)

Film thickness	D band		G band		I(D)/I(G)
	Position	FWHM	Position	FWHM	
	w_D (cm^{-1})	Δw_D (cm^{-1})	w_G (cm^{-1})	Δw_G (cm^{-1})	
DLC 200 nm	1342.4	254.29	1537.3	150.58	0.329
DLC 400 nm	1338.9	263.27	1538.2	150.64	0.340
DLC 600 nm	1350.8	245.66	1541.6	147.28	0.346
DLC 740 nm	1351	264.23	1540.3	149.55	0.357
DLC 870 nm	1359.5	252.72	1543.9	141.57	0.387

scratching tracks made in each sample are 5000 µm and the maximum load is 1000 mN. Five different thicknesses (200 nm, 400 nm, 600 nm, 740 nm and 870 nm) of DLC were deposited

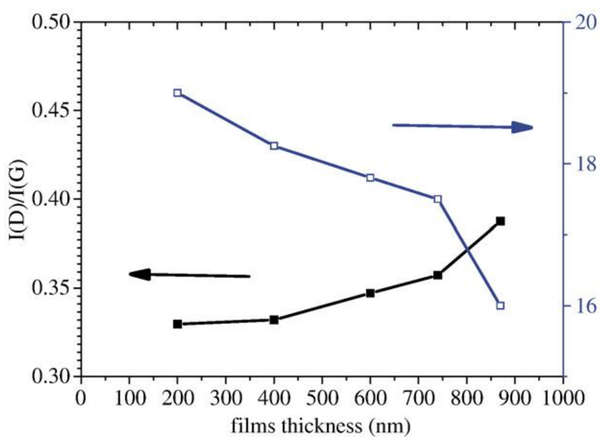

Fig. 3. The I(D)/I(G) ratio and nano-hardness of DLC on silicon substrate in different film thickness.

on different interlayer/substrate systems to study the film thickness effect.

3. Results and discussion

3.1. The film thickness effect on adhesion

The strength of adhesion of DLC on different interlayer/substrate systems has been examined by optical microscope and is estimated qualitatively by the peeling degree and area in each film. For brevity, only two thicknesses are presented here. Fig. 1 displays the micrographs of the three different samples (DLC/Si, DLC/Cr/Si and DLC/Ti/Si) with film thickness 200 nm. The arrows A and B indicate the peeling area and good adhesion area, respectively. As shown in Fig. 1, the peeling degree of DLC on interlayer titanium is worse than that on interlayer chromium. For thicker DLC film, Fig. 2 shows the micrographs of another three samples with film thickness 870 nm. For larger film thickness, DLC on both interlayers does not exhibit good adhesion, even though DLC on interlayer chromium has slightly more good adhesion area. For films with the same thickness, the peeling degree for DLC on interlayer titanium is always worse than that on interlayer chromium. Furthermore, as the film thickness increases, the degradation of the film tends to increase for DLC on both interlayers. To examine the film thickness effect, the bonding structure of DLC on silicon substrate without interlayer was examined via Raman spectroscopy and the data is listed in Table 1. As the film thickness increases, the G shift and I(D)/I(G) ratio increases. The increase of G shift and I(D)/I(G) ratio means the decrease of sp^3 fraction and increase of sp^2 fraction [12]. For mechanical property, the hardness of each film thickness was measured by nanoindentation and the

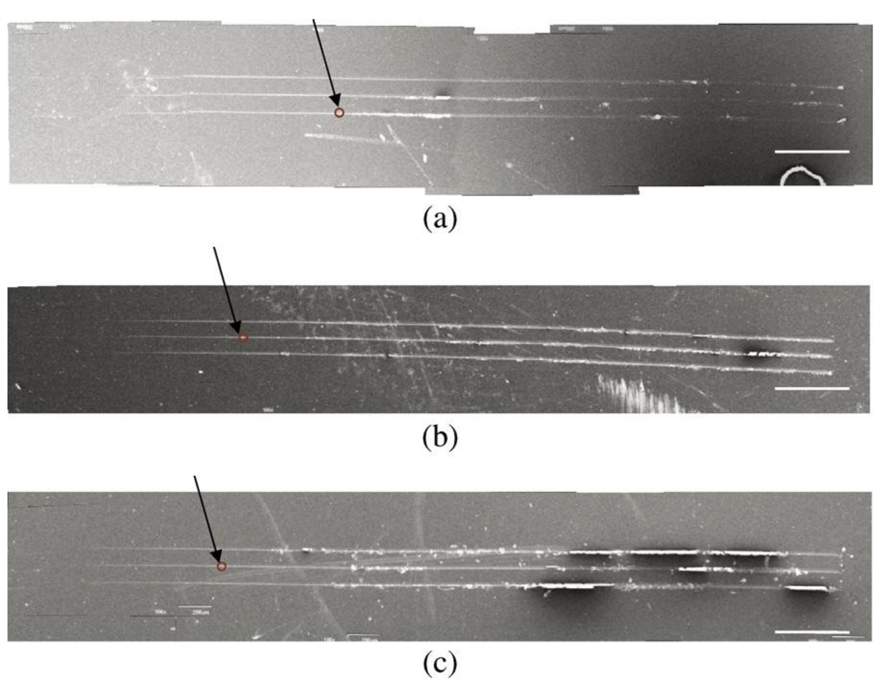

Fig. 4. Optical micrographs for scratch tracks of DLC films deposited on Cr interlayer with thickness (a) 200 nm, (b) 400 nm, and (c) 600 nm. The length of the scale bar is 500 µm. The arrow indicated where the critical load is recorded.

correlation with I(D)/I(G) ratio is shown in Fig. 3. The figure shows that as the film thickness increases, the hardness decreases and the I(D)/I(G) ratio increases. Previous studies has suggested the harder the substrate, the better the film adhesion to the substrate [13,14]. Our results show a similar trend.

The film thickness on adhesion strength was quantitatively measured by nanoscratch on DLC/Cr/Si for three film thickness samples. Fig. 4(a)–(c) depicts the optical micrographs of each test. Three scratches were made for each load on different locations in each sample for good statistics. The arrow marks the onset of cracks by the abrupt change of the friction

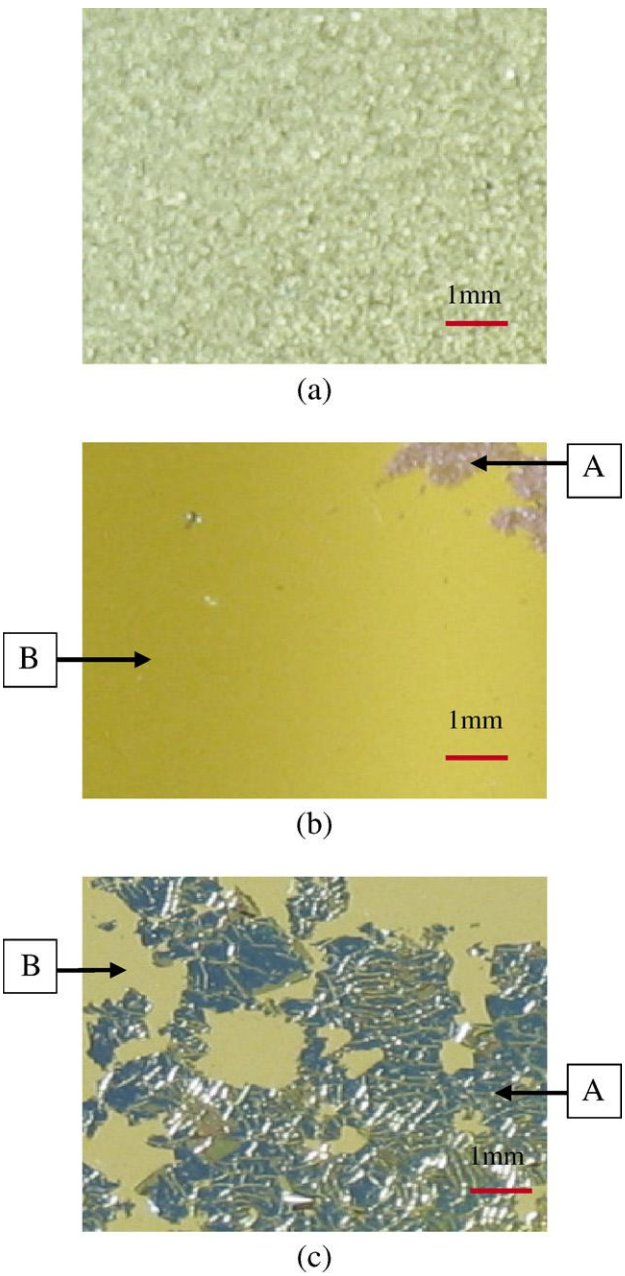

Fig. 5. The micrographs of 200 nm DLC with 40 nm interlayer (a) DLC/glass, (b) DLC/Cr/glass, and (c) DLC/Ti/glass. The arrow A indicates the peeling region and arrow B indicates the good adhesion region.

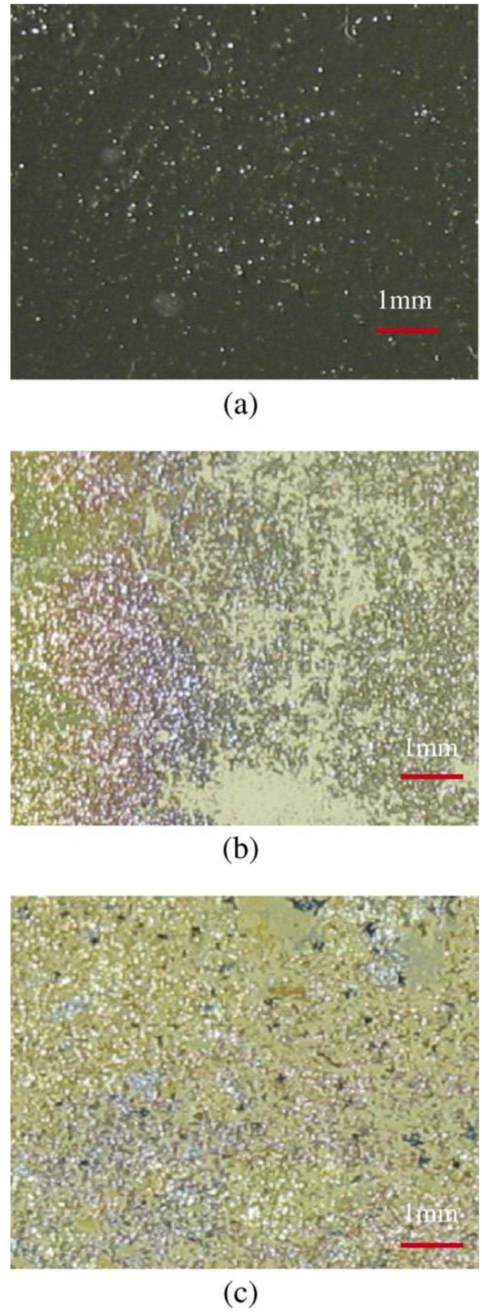

Fig. 6. The micrographs of 870 nm DLC with 40 nm interlayer (a) DLC/glass, (b) DLC/Cr/glass, and (c) DLC/Ti/glass.

coefficient and the critical load was recorded. The critical load for film thickness 200 nm, 400 nm, 600 nm was 265 mN, 130 mN and 95 mN, respectively. For thicker film sample, not only did the delamination occur early but the spalling degree became worse as the loading increased. This demonstrates that the increase of film thickness impairs the film adhesion.

3.2. The substrate and interlayer effect on adhesion

The substrate effect was investigated by depositing the same film thickness on glass substrate (Corning 1737). Figs. 5 and 6 show the micrographs DLC film on glass with chromium or

Table 2
Different area Raman spectra of 200 nm DLC film with 40 nm interlayer Cr on silicon substrate (A: peeling area, B: good adhesion area)

Area	D band		G band		I(D)/I(G)
	Position	FWHM	Position	FWHM	
	w_D (cm^{-1})	Δw_D (cm^{-1})	w_G (cm^{-1})	Δw_G (cm^{-1})	
A	1362.8	275.86	1539.1	146.61	0.481
B	1358.3	275.46	1546.4	159.24	0.362

Table 4
Thermal coefficient of expansion of various materials at room temperature

	TCE
Glass [20]	4.2 μm m^{-1} K^{-1}
Ti [21]	8.6 μm m^{-1} K^{-1}
Cr [21]	4.9 μm m^{-1} K^{-1}
Si [21]	3.2 μm m^{-1} K^{-1}
DLC [21]	2.3 μm m^{-1} K^{-1}

titanium as interlayer with thickness 200 nm and 870 nm, respectively. For small film thickness 200 nm, DLC/Cr/glass had better adhesion than that in DLC/Cr/Si. The improvement in adhesion for changing substrate does not apply for interlayer titanium. As the film thickness increases from 200 nm to 870 nm, the peeling degree of the film deteriorated for both metal interlayers on glass substrate. This also applies to the silicon substrate and this phenomenon is attributed to the increase of the film thickness. The samples of 200 nm thickness is further investigated by comparing the bonding structure in peeling region and good adhesion region for interlayer chromium on silicon substrate (Fig. 1b) and glass substrate (Fig. 5b). The Raman spectra data is listed in Tables 2 and 3. For good adhesion area (marked B) on both substrates, the I(D)/I(G) ratio is similar in magnitude. It seems the bonding structure for films with good adhesion may not differ much. There are various mechanisms to explain why DLC/Cr/glass has better adhesion strength than DLC/Cr/Si for small film. One possibility might be the residual stress which composed of thermal stress and intrinsic stress. While the intrinsic stress is related to the microstructure such as lattice distortion and is difficult to measure, the thermal stress can be estimated by the coefficient of thermal expansion (CTE) multiplied by temperature difference. For illustration, the CTE of DLC, chromium, titanium, silicon and glass, is listed in Table 4. From that table, the CTE of chromium is similar to that of glass. Consequently, for DLC deposition on interlayer chromium over glass substrate will have smaller thermal stress than that over silicon substrate. In the same way, for DLC deposition on high CTE mismatch interlayer titanium, the high compressive stress is detrimental to film adhesion.

For peeling area (marked A) where there is some debris left, the bonding structure of the debris was examined by Raman spectra. The ratio of I(D)/I(G) is high (0.732 for glass, 0.481 for silicon) in these areas compared to those in good adhesion areas. This high I(D)/I(G) ratio implies high sp^2 concentration [12]. The intrinsic compressive stress has been shown to increase with increasing concentration of sp^2 bonding [15] and deposition time [16]. Based on these studies and our results, there seem to be some correlations among residual stress, sp^2 concentration and film thickness. Other than residual stress, other factors might also contribute to the peelings. Since the adhesion strength of metal interlayer/substrate interface is stronger than that of DLC/metal interlayer interface, the peeling of DLC seems to occur after metal interlayer deposition. As a result, surface effects on metal interlayer like oxidization and carburization are possible mechanisms that lead to peeling phenomenon [17–19]. The oxide on titanium, steel substrates has been shown to impair the adhesion of DLC films [17]. Therefore, the oxidization on metal interlayer might be another factor that leads to the peeling of the films. While the oxidization impairs the adhesion strength, the carburization of certain metals has shown to promote the adhesion of the diamond films on metal substrates [16]. The nitridation and carburization of Cr has been shown to affect the nucleation of diamond films with substrate temperature 800 °C [16]. Even though the substrate temperature in our current study is moderate, for very thin layer specimen, the role of carburization cannot be neglected. Based on the improving adhesion of very thin DLC film on interlayer chromium and poor adhesion for DLC on interlayer titanium, the carburization might be more preferable in interlayer chromium than in interlayer titanium. The details of oxidization and carburization on each metal interlayer and the associated microstructure need further investigation like XRD and Auger depth profile measurement. This is currently under study.

Table 3
Different area Raman spectra of 200 nm DLC film with 40 nm interlayer Cr on glass substrate (A: peeling area, B: good adhesion area)

Specimen	D band		G band		I(D)/I(G)
	Position	FWHM	Position	FWHM	
	w_D (cm^{-1})	Δw_D (cm^{-1})	w_G (cm^{-1})	Δw_G (cm^{-1})	
A	1380.6	289.50	1553.0	122.19	0.732
B	1358.2	285.18	1546.3	158.89	0.383

4. Conclusions

In this study, various thicknesses of DLC films were deposited on silicon and glass with interlayers chromium and titanium. The adhesion was analyzed by OM inspection, nanoindentation, and nanoscratch. The results are summarized as follows:

1. As the film thickness increases, the I(D)/I(G) rate increases and the hardness decreases. The increase of I(D)/I(G) ratio means the decrease of sp^3 contents and tends to increase the peeling degree of the films. The Raman spectra for peeling area with high I(D)/I(G) ratio confirm this hypothesis. Nanoscratch test shows the spalling of the thicker film initiated earlier with a smaller critical load describes the same phenomenon.
2. In very thin film thickness (200 nm), the adhesion strength for DLC on interlayer chromium over glass substrate is better

than that on silicon substrate. The smaller thermal residual stress due to less mismatch of CTE between chromium and glass might be the reason.

3. For same substrate and identical film thickness, DLC on interlayer chromium has less peeling area and more good adhesion area than that on interlayer titanium. High thermal residual stress results from large CTE mismatch and the associated high sp^2 contents are possible explanations.
4. Other mechanisms on metal interlayers also contribute to the peeling of the films. Oxidation which impairs the adhesion and carburization which promotes the adhesion are important factors that need to be considered. Based on the improving adhesion of very thin DLC film on interlayer chromium and poor adhesion for DLC on interlayer titanium, the carburization might be more preferable in interlayer chromium than in interlayer titanium.

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