# The Effect of Bonding Structure of Diamond Like Carbon (DLC) Film with Surface Nickel Coating upon Laser Annealing

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***Abstract*-Previous work has shown that the bonding structure and phase of amorphous carbon (a-C) can be modified by laser annealing. In this work, the effect of surface modification by metal coating on a-C during laser annealing was studied. A-C film was deposited by the filtered cathodic vacuum arc (FCVA) technique onto n-type (100) silicon substrate at room temperature. Nickel (Ni) was deposited on the surface of a-C films by electron beam (e-beam) evaporation method, and laser annealing with different laser energy density was performed on the a-C films with and without Ni coating. Visible Raman spectroscopy was used to examine the bonding structure evolution upon laser annealing and the effect on the bonding structure of a-C by introducing Ni onto the DLC film surface. The Raman spectra shows more pronounced change for a-C films with Ni coating than those without Ni coating upon laser annealing, and the Raman features also suggest that the Ni surface coating can enhance formation of the six-ring graphitic-like sp2 ordering. Electrical measurement shows a low resistive characteristic for both set of films due to laser induced conducting sp2 clusters formation.**

***Keywords-Amorphous Carbon;Graphitization; Laser Annealing; Visible Raman Spectroscopy***

## I. INTRODUCTION

Amorphous carbon(a-C) has attracted a lot of attention due to its wide range of physical properties in past decades. One of the most interesting features is its ability to have highly contrasting properties when its sp2 and sp3 content change to exhibit graphite like or diamond like properties respectively. A-C with significant fraction of sp3 bonds (75~85 %), is known as tetrahedral carbon (ta-C) or diamond like carbon (DLC) [1], which has excellent mechanical properties, chemical inertness, optical transparency and smooth surface [2-5]. It can be widely adopted in a variety of applications such as MEMS devices, automotive parts, optical windows and storage disks. In contrast to ta-C, a-C with a high fraction of sp2 bonds tends to have properties more similar to graphite [1]. Recently, our group has reported a novel form of carbon film with high crystalline sp2 content named as textured carbon, which has graphitic-like planes aligned perpendicular to the substrate. One of the superior properties of textured carbon film is its high electrical conductivity, ease of deposition, low temperature deposition and conformity to substrate makes it promising in electronic applications[2, 6-8].

Textured carbon can be deposited by applying sufficient energy to the $C^+$ ions during film deposition, which in this context is by supplying a suitable substrate bias, growth temperature or ion flux [6, 8]. In this respect, these are defined as in-situ methods. Another way of obtaining textured carbon is via post annealing of a-C film using techniques such as thermal and laser annealing [2, 7, 9-10]. All these methods convert sp3 bonds into graphitic-like sp2 bonds. Previous work has also shown that the sp3 to sp2 transformation can be induced by incorporating metallic atoms into the film[11-13]. One of the common metals is nickel (Ni), which can be deposited in-situ by co-sputtering [14], hybrid plasma enhance vapor deposition (PECVD)[15], or filtered cathodic vacuum arc technique (FCVA) [11, 16]. However the there is still lack of ex-situ method to introduce Ni atom into carbon film. Nickel silicide formation has been shown by coating Ni on top of silicon, and annealed by thermal heating or laser. This is realized because the Ni is melted and diffuse into silicon [17]. In this work, ex-situ method—introducing surface coated Ni by laser annealing is demonstrated. The enhancement of graphitic-like sp2 bonds formation is shown by visible Raman spectroscopy, and the electrical property of the Ni coated C film after laser annealing is also investigated.

## II. EXPERIMENTAL

The a-C films were prepared via FCVA on (100) n-type Si wafer at room temperature. Before film deposition, the Si wafer was firstly cleaned using acetone, followed by ultrasonic with isopropanol (IPA) to remove any possible surface particles. Next, a titanium (Ti) layer with a thickness of 50nm was deposited using Denton Electron beam (E-Beam) evaporation on the Si substrate. This metal layer serves as the bottom electrode for electrical measurement at a later stage. The cathode target used in the FCVA is a 99.999% pure graphite rod. The deposition was carried out at a vacuum level no higher than $3x10^{-6}$Torr and at room temperature. A pulse substrate bias of -70V was applied to the substrate during the deposition to obtain the as-deposited a-C film. The a-C film was deposited on the Ti with 3mm periodic spacing with a portion of the Ti covered by thermal tape as a shadow mask. Two sets of sample are used, namely: (1) Pure a-C film (2) a-C film with a layer of Ni thin film on top. The thickness of deposited a-C films was measured to be 100nm by Tencor P10 surface profiler meter, and Ni film on a-C film was deposited with a thickness of 15nm.

A 248 nm KrFExcimer-Laser with pulse duration of 23nm, and 50 pulses was used to anneal the samples in ambient condition. The spatial energy distribution of the laser pulse has a uniform near flat-top energy profile [18]. WITecvisible Raman spectroscopy with a 532 nm Diode-pumped Solid State Laser was used to study the effect of Ni coating on the C film microstructure during laser annealing. The resultant Raman spectra were then fitted using a Breit-Wigner-Fano (BWF) line shape for the G band. In addition, a Lorentzian line shape was used for the D band when the spectra cannot be fitted by a single BWF line shape.

The electrical IV characterization measurement was performed by using a two point probing method. The test structure which consists of a sandwiched Ti-C-Ti structure is illustrated in Fig. 1. The top and bottom metal electrode used has a thickness of 50 nm, and the diameter of top Ti electrode is 500um. A cascade 200-nm probe station with a Hewlett Packard 4156A precision semiconductor parameter analyzer, with voltage sweep from -2V to 2V and a voltage step size of 0.01 V was used for the electrical characterization.

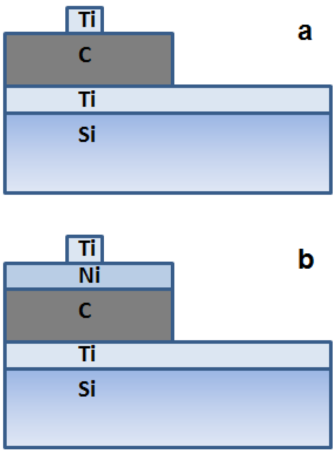


Fig.1 Schematic of the electrical test structure—Metal-Carbon-Metal structure

## III. RESULTS AND DISCUSSION

### A. *Micro structural study by Raman spectroscopy*

Fig. 2 (a) and (b) show the Raman spectra of the two types of a-C film before and after laser annealing with different laser energy densities. There are two prominent signature Raman peaks for a-C film—one is known as the G peak which is the vibrational response of the stretching mode of sp2 bonds and it represents all sp2 bonds within the film (both the ring-like and chain-like [19], whereas the other one is the D peak which refers to the breathing mode of sp2 bonds in the form of six-ring like (graphitic like) [19]. The G peak normally locates between 1500—1630cm$^{-1}$, while D peak appears at around 1355cm$^{-1}$. From the Raman spectra, the main changes upon laser annealing are the shift of G peak position and the appearance of the D peak. By comparing Fig. 2 (a) and (b), it is observed that the changes in D peak aremore sensitive to laser energy for the sample which has a Ni coating on the a-C film.

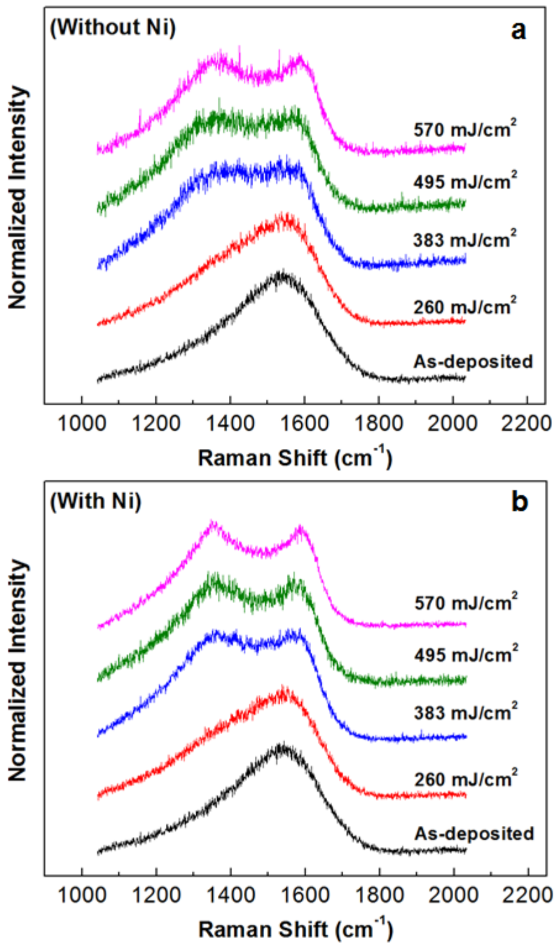


Fig. 2 Raman spectra of a-C film before and after laser annealing with different laser energy density (a) pure a-C film, and (b) a-C film with Ni layer coated on top

To confirm this observation, all the Raman spectra were fitted with BWF or Lorentzian, and the major Raman features—G peak position and I(D)/I(G) ratio were obtained and shown in Fig.3 (a) and (b). As the laser energy density increases, the G peak tends to move towards a higher wavenumber which indicates the decrease in fraction of sp3 bonds, and the formation of more six-ring like sp2 clusters [19, 20]. Moreover the I(D)/I(G) ratio increases with laser energy density, which implies that the average size of six-ring like sp2 clusters has increased [19, 20]. The size of the clusters can be calculated using the equation below [19]:

$$\frac{I(\mathrm{D})}{I(\mathrm{G})} = C_{\lambda}' L_{a}^{2} \quad (1)$$

Where La is the sp2 cluster size and $C_{\lambda}'$ is a constant value which is dependent on the wavelength of the Raman spectroscopy system. Here $C_{\lambda}$'$=0.0055Å$when the system has a wavelength (λ) of 532nm. Table 1 shows the average cluster sizes calculated based on the I(D)/I(G) ratio extracted from Raman spectra.

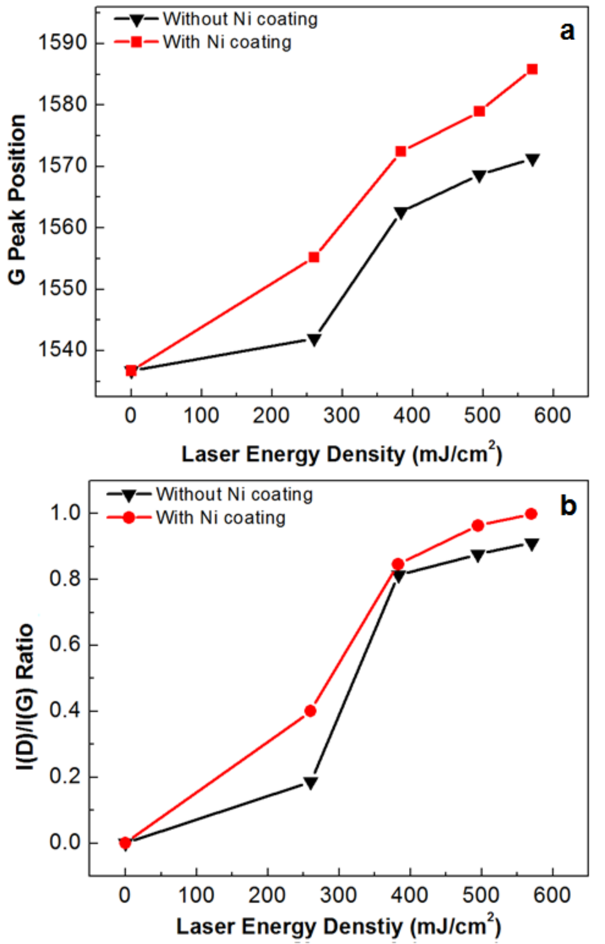


Fig. 3 (a) G peak position with respect to change of laser energy density, and (b) I(D)/I(G) ratio with respect to change of laser energy density

TABLEISP2 CLUSTER SIZE WITHIN A-C FILM BEFORE AND AFTER LASER ANNEALING WITH DIFFERENT ENERGY DENSITY

| Laser Energy Density (mJ/cm2) | La (Å) (without Ni) | La (Å) (with Ni) |
|---|---|---|
| 0 | 0 | 0 |
| 260 | 5.38 | 10.73 |
| 383 | 12.16 | 12.93 |
| 495 | 12.63 | 13.36 |
| 570 | 12.88 | 13.50 |

Laser annealing has been shown to be a possible way to reduce the high compressive stress of C film, which is realized through a conversion of sp3 bonding to sp2 bonding [10, 21]. These sp2 bonds are six-ring graphitic like, and ordered in the preferred orientation as a response to the high compressive stress realization during film deposition. The overall trend is similar for both films with and without Ni coating; the G peak position increases with the laser energy density used in the annealing. Since G band is only sensitive to sp2 bonding, the higher the G peak wavenumber, means more sp2 bonding sites are energized during the Raman scattering [19]. Similarly, an increased laser density promotes the increase in I(D)/I(G) ratio, because of the increase in the amount and average size of graphitic sp2 clusters. These sp2 clusters will serve as the electrical conducting path for the low electrical conductivity. Previous work has suggested that the graphitization process can be enhanced by incorporating metal such Ni [14, 22-25], which can be used to explain the different graphitization rate between these two types of films upon laser annealing. The more obvious change in Raman features for the film with Ni coating is believed to be caused by the presence of Ni atom within the film. This is same as the formation of Ni silicide process, during laser annealing, the heat induced is able to melt the Ni film [17, 26-27], and some Ni atoms can diffuse into C film, hence more and larger graphitic like sp2 clusters are able to form.

### B. *Electrical measurement*

The electrical properties of the two types of film before and after laser annealing are determined by DC IV measurement shown in Fig. 4. It is observed that at a low laser energy density of 260 mJ/cm$^2$, the film exhibits a very high electrical resistivity. This is because the film is mainly amorphous in nature due to the low laser energy which does not result in any material change. This result tallies with the Raman results which indicate that there are few sp2 clusters formed. At the laser energy level of 383 mJ/cm$^2$, the film exhibits a much lower resistivity due to the formation of conducting sp2 clusters. This result is again confirmed by the Raman spectrum which shows a D peak indicating much larger conducting sp2 clusters present within the film. The total resistance measured for the a-C film with Ni coating is lower as compared to the a-C film without Ni coating after subjecting to laser annealing at 383 mJ/cm$^2$. However when the energy density continues increasing, the a-C film without Ni exhibit a lower total resistance than that of the a-C film with Ni film although the conductivity for both set of films increases. This is because the fact that the laser energy is sufficient to fully induce the sp3 to graphitic sp2 clusters transformation, and the resistance of remaining Ni on C surface cannot be neglected and this increases the total resistance of film with Ni coating.

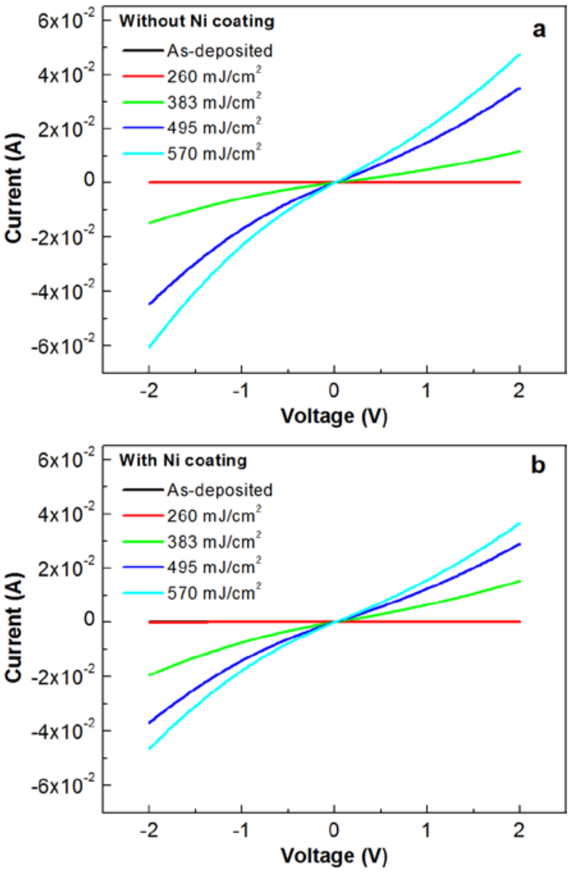


Fig. 4 IV characteristic of a-C film before and after laser annealing with different laser energy density (a) pure a-C film, and (b) a-C film with Ni layer coated on top

## IV. CONCLUSIONS

It has been shown that at low laser energy density of 260 mJ/cm$^2$, there is no phase change in the a-C film and this is verified via the Raman spectrum. However above a laser energy density of 383 mJ/cm$^2$, the conversion from a-C film to textured film occurs. The G peak position in the Raman spectra of the a-C film moves towards a higher wavenumber due to the decrease in the fraction of sp3 bonds and this implies the formation of more six-ring like sp2 clusters. The I(D)/I(G) ratio increases with increasing laser energy density due to the increase in the average size of the sp2 clusters. The presence of Ni coating on a-C film surface enhances the graphitization during laser annealing, which is believed to be realized through diffusion of Ni atom into a-C film. There is an advantage of Ni on a-C film at low laser energy density resulting in the improvement of electrical conductivity. However, the Ni film has a negative effect on the electrical conductivity at higher laser energy density.


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## REFERENCES


[1] J. Robertson, "Diamond-like amorphous carbon,"*Materials Science & Engineering R-Reports*, vol. 37, pp. 129-281, May 2002.

[2] N. Xu, *et al.*, "Electrical properties of textured carbon film formed by pulsed laser annealing,"*Diamond and Related Materials*, vol. 23, pp. 135-139, 2012.

[3] P. D. Maguire, *et al.*, "Mechanical stability, corrosion performance and bioresponse of amorphous diamond-like carbon for medical stents and guidewires,"*Diamond and Related Materials*, vol. 14, pp. 1277-88, 2005.

[4] J. K. Luo, *et al.*, "Diamond and diamond-like carbon MEMS,"*Journal of Micromechanics and Microengineering*, vol. 17, pp. 147-63, 2007.

[5] A. C. Ferrari, "Diamond-like carbon for magnetic storage disks," in *Symposium G on Protective Coatings and Thin Films, of the E-MRS 2003 Spring Conference, 10-13 June 2003*, Switzerland, 2004, pp. 190-206.

[6] C. W. Tan, *et al.*, "Microstructure and through-film electrical characteristics of vertically aligned amorphous carbon films,"*Diamond and Related Materials*, vol. 20, pp. 290-293, 2011.

[7] M. Shakerzadeh, *et al.*, "Field emission enhancement and microstructural changes of carbon films by single pulse laser irradiation,"*Carbon*, vol. 49, pp. 1018-1024, 2011.

[8] M. Shakerzadeh, *et al.*, "Plasma density induced formation of nanocrystals in physical vapor deposited carbon films,"*Carbon*, vol. 49, pp. 1733-1744, 2011.

[9] S. C. Ray, *et al.*, "Orientation of graphitic planes during annealing of "dip deposited" amorphous carbon film: A carbon K-edge X-ray absorption near-edge study,"*Carbon*, vol. 44, pp. 1982-5, 2006.

[10] D. G. McCulloch, *et al.*, "Mechanisms for the behavior of carbon films during annealing,"*Physical Review B*, vol. 70, Aug 2004.

[11] P. Zhang, *et al.*, "Rapid thermal annealing study on the metal containing amorphous carbon films,"*Diamond and Related Materials*, vol. 12, pp. 2093-2098, Oct-Nov 2003.

[12] Y. H. Lin, *et al.*, "Annealing effect on the structural, mechanical and electrical properties of titanium-doped diamond-like carbon films,"*Thin Solid Films*, vol. 518, pp. 1503-1507, Dec 2009.

[13] A. T. T. Koh, *et al.*, "Structural characterization of dual-metal containing diamond-like carbon nanocomposite films by pulsed laser deposition,"*Diamond and Related Materials*, vol. 19, pp. 637-642.

[14] G. J. Kovács, *et al.*, "X-ray photoelectron spectroscopic study of magnetron sputtered carbon-nickel composite films,"*Thin Solid Films*, vol. 516, pp. 7942-7946, 2008.

[15] W. Dai, *et al.*, "Microstructure and property evolution of Cr-DLC films with different Cr content deposited by a hybrid beam technique,"*Vacuum*, vol. In Press, Corrected Proof.

[16] Y. B. Zhang, *et al.*, "Carbon nanotubes grown on cobalt-containing amorphous carbon composite films,"*Diamond and Related Materials*, vol. 15, pp. 171-175, 2006.

[17] Y. Setiawan, *et al.*, "Nickel silicide formation using multiple-pulsed laser annealing,"*Journal of Applied Physics*, vol. 101, Feb 2007.

[18] X. C. Wang, *et al.*, "Fabrication of silicon nanobump arrays by near-field enhanced laser irradiation,"*Applied Physics Letters*, vol. 96, Feb 2010.

[19] A. C. Ferrari and J. Robertson, "Interpretation of Raman spectra of disordered and amorphous carbon,"*Physical Review B*, vol. 61, p. 14095, 2000.

[20] R. Kalish, *et al.*, "Thermal stability and relaxation in diamond-like-carbon. A Raman study of films with different sp3 fractions (ta-C to a-C),"*Applied Physics Letters*, vol. 74, pp.

2936-2938, 1999.

[21] D. R. McKenzie, *et al.*, “Compressive-stress-induced formation of thin-film tetrahedral amorphous carbon,”*Physical Review Letters,* vol. 67, p. 773, 1991.

[22] G. J. Kovács, *et al.*, “Raman spectroscopic study of magnetron sputtered carbon-nickel and carbon nitride-nickel composite films: The effect of nickel on the atomic structure of the C/CNx matrix,”*Thin Solid Films,* vol. 516, pp. 7910-7915, 2008.

[23] R. Koppert, *et al.*, “Nickel containing diamond like carbon thin films,”*Solid State Sciences,* vol. 11, pp. 1797-1800, 2009.

[24] G. Abrasonis, *et al.*, “Growth regimes and metal enhanced 6-fold ring clustering of carbon in carbon-nickel composite thin films,”*Carbon,* vol. 45, pp. 2995-3006, 2007.

[25] P. VijaiBharathy, *et al.*, “Effect of nickel incorporation on structural, nanomechanical and biocompatible properties of amorphous hydrogenated carbon thin films prepared by low energy biased target ion beam deposition,”*Thin Solid Films,* vol. 519, pp. 1623-8, 2010.

[26] R. F. Wood, *et al.*, “Macroscopic theory of pulsed-laser annealing. II. Dopant diffusion and segregation,”*Physical Review B,* vol. 23, pp. 5555-5569, 1981.

[27] A. T. Y. Koh, *et al.*, “Pulsed Laser Annealing of Silicon-Carbon Source/Drain in MuGFETs for Enhanced Dopant Activation and High Substitutional Carbon Concentration,”*Electron Device Letters, IEEE,* vol. 29, pp. 464-467, 2008.