Fabricating functionally graded films with designed gradient profiles using pulsed laser deposition

Yoo Jai Won and Hyungson Ki

Citation: J. Appl. Phys. 113, 174910 (2013); doi: 10.1063/1.4803692
View online: http://dx.doi.org/10.1063/1.4803692
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v113/i17
Published by the AIP Publishing LLC.
Fabricating functionally graded films with designed gradient profiles using pulsed laser deposition

Yoo Jai Won and Hyungson Ki
School of Mechanical and Advanced Materials Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Gyeongnam 689-798, South Korea

(Received 11 April 2013; accepted 15 April 2013; published online 7 May 2013)

A novel picosecond-laser pulsed laser deposition method has been developed for fabricating functionally graded films with pre-designed gradient profiles. Theoretically, the developed method is capable of precisely fabricating films with any thicknesses and any gradient profiles by controlling the laser beam powers for the two different targets based on the film composition profiles. As an implementation example, we have successfully constructed functionally graded diamond-like carbon films with six different gradient profiles: linear, quadratic, cubic, square root, cubic root, and sinusoidal. Energy dispersive X-ray spectroscopy is employed for investigating the chemical composition along the thickness of the film, and the deposition profile and thickness errors are found to be less than 3% and 1.04%, respectively. To the best of the authors’ knowledge, this is the first method for fabricating films with designed gradient profiles and has huge potential in many areas of coatings and films, including multifunctional optical films. We believe that this method is not only limited to the example considered in this study, but also can be applied to all material combinations as long as they can be deposited using the pulsed laser deposition technique.

© 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4803692]

I. INTRODUCTION

Thin film deposition has become an indispensable tool in many areas of science and technology. In this process, physical properties of a substrate, such as optical, electrical, or mechanical properties can be modified by applying a thin film of a desired material on the surface of the substrate. Especially, as far as mechanical properties are concerned, we can impart to a substrate virtually any property that is not intrinsically owned by the substrate material, such as hardness, corrosion resistance, lubricity, and chemical inertness. Among many deposition techniques, pulsed laser deposition (PLD) is regarded as one of the most capable physical vapor deposition methods because materials with complex stoichiometry can be ablated and deposited by using a high intensity laser.

One important research topic in pulsed laser deposition is the fabrication and use of functionally graded films. This is a popular technique to fabricate a film with advanced and/or improved functionality by designing a film with more than one material. For example, interlayer and multilayer techniques have been used to improve the adhesion strength of diamond-like carbon (DLC) films. As well known, a large internal compressive stress exists in DLC films regardless of the growth technique, and the film starts to peel off from the substrate when this large compressive stress reaches a certain level. Therefore, DLC films are generally limited to a thickness of 0.1–0.2 μm. This kind of techniques are not limited to adhesion problems but also are actively employed to enhance other properties. For instance, Wei et al. doped DLC films with Cu, Ti, or Si by a sequential pulsed laser deposition of two targets to investigate electrical properties, wear resistance characteristics, and infrared range optical properties. Recently, Cho et al. has developed a pulsed laser deposition technique to build a functionally gradient DLC film (FGDLC) on a stainless steel substrate, where the DLC content increases gradually from the substrate surface to the film outer surface. Much improved adhesion strength was reported, but in that method, a gradient profile was not controlled precisely. Apparently, if it were possible to deposit a graded film with a pre-designed gradient profile, we could fine-tune the performance of the film and also made films with more advanced functionalities. Unfortunately, however, this kind of deposition method has not been available to the best of the authors’ knowledge.

In this study, a novel pulsed laser deposition method is proposed for building a functionally graded film with a designed gradient profile. Based on Cho et al.’s PLD method, a scheme to fabricate a film of any thickness and gradient profile has been developed. In this method, a 355 nm picosecond laser beam is split into two beams, each of which is controlled individually by a motorized beam attenuator. Two beams are irradiated on two different targets, respectively, and the produced dissimilar plasmas are mixed in space before they are deposited on the substrate. We have successfully developed a scheme to generate laser power profiles for both targets from the content profile functions of the two materials. As an implementation example, FGDLC films with six different gradient profiles have been fabricated, and the thicknesses and content profiles of the deposited films agreed very well with the original designs. To the best of the authors’ knowledge, this is the first method for precisely fabricating films with designed gradient profiles.
We believe that this method is not limited to DLC-stainless steel films, but can be applied to all material combinations as long as they can be deposited using the pulsed laser deposition technique.

II. EXPERIMENTAL METHOD

The experimental setup is shown schematically in Figure 1, which is basically the same as the one used in Ref. 16. A 355 nm, 6 W picosecond laser (Coherent Talisker 355-4) with a pulse energy of up to 30 μJ is used as an energy source. The pulse repetition rate is 200 kHz, and the pulse width is 10–15 ps. The laser beam is split into two beams using a beam splitter, and each split beam passes through a motorized beam attenuator. These attenuators are connected to a PC through a controller and are controlled by a developed LabVIEW program, which integrates the laser shutter, the two attenuators, and the controller. In this way, the intensity of each split beam can be varied with time individually. When the laser shutter is opened, the two attenuators operate simultaneously. As schematically shown in Figure 1, two dissimilar plasma plumes from two different targets are mixed uniformly before they are deposited onto the substrate. Because the composition of the mixed plasma plume can be changed over time by programming the attenuators, functionally gradient films or coatings can be deposited. The incident angles of both beams are 53°. Plasma plumes ablated from both targets are observed using an intensified charge-coupled device (ICCD) camera.

The objective of this study is to build a functionally graded film with a designed gradient profile using the afore-mentioned pulsed laser deposition method. As an implementation example, in this study, a functionally graded DLC film built on a stainless steel 316 L substrate was considered. Figure 2 shows a stainless steel 316 L target, a 99.99% purity graphite target, and a polished stainless steel 316 L substrate. Stainless steel substrates were polished with 400, 800, and 1200 grit sandpapers, and then finished with 1 μm polycrystalline diamond polishing suspension. After polishing, they were cleaned in an ultrasonic bath for 10 min to remove remaining suspension particles. Figure 3 shows an ICCD camera image taken during the deposition process. As clearly seen, the two plumes were mixed before they were deposited on the substrate.

Figure 4 shows a schematic diagram of a FGDLC film of thickness \( L \) that we want to build, where the gradient profiles for DLC and stainless steel 316 L in the thickness direction are represented by content profile functions, \( \tilde{c}_{DLC}(x) \) and \( \tilde{c}_{SUS}(x) \), respectively. Here, content profile functions are defined on the basis of particle numbers. They can be arbitrary functions varying between 0 and 1, and \( x \) is the coordinate measured from the surface of the substrate in the thickness direction. Also, it is obvious that \( \tilde{c}_{DLC}(x) + \tilde{c}_{SUS}(x) = 1 \) at any point in the film. Note that in this deposition method, we control the laser powers for the two targets using the attenuators to vary the deposition rates of both materials with time. Therefore, in order to build a designed gradient profile as schematically shown in Figure 4, we need to calculate the laser power profiles for the two target materials (i.e., \( P_{DLC}(t) \) and \( P_{SUS}(t) \)) that give rise to the designed content profile functions, \( \tilde{c}_{DLC}(x) \) and \( \tilde{c}_{SUS}(x) \).

In actual deposition processes, however, it is much more convenient to use content profile functions based on the...
actual deposition thicknesses, \( c_{\text{DLC}}(x) \) and \( c_{\text{SUS}}(x) \), which can be easily calculated as follows:

\[
\begin{align*}
  c_{\text{DLC}}(x) &= \frac{V_{m,\text{DLC}} c_{\text{DLC}}(x)}{V_{m,\text{DLC}} c_{\text{DLC}}(x) + V_{m,\text{SUS}} c_{\text{SUS}}(x)}, \\
  c_{\text{SUS}}(x) &= \frac{V_{m,\text{SUS}} c_{\text{SUS}}(x)}{V_{m,\text{DLC}} c_{\text{DLC}}(x) + V_{m,\text{SUS}} c_{\text{SUS}}(x)}.
\end{align*}
\]

Here, \( V_{m,\text{DLC}} \) and \( V_{m,\text{SUS}} \) are molar volumes (cm\(^3\)/mol) of DLC and stainless steel films, which must be determined experimentally. In our experiment, \( V_{m,\text{DLC}} \) and \( V_{m,\text{SUS}} \) were measured to be 6.17 and 6.57 cm\(^3\)/mol, respectively.

Figure 5 is a schematic diagram of a FGDLC film defined by content profile functions based on film thicknesses, \( c_{\text{DLC}}(x) \), and \( c_{\text{SUS}}(x) \).

Suppose that we want to build a film of thickness \( L \) in a total deposition time of \( T \), and that \( T \) is divided into \( n \) number of time steps, \( \Delta t \), where \( n \) is a large enough number to create a smooth gradient profile. Also, let \( \xi \) denote the instant film thickness while the film is being built, then \( \xi \) increases from 0 to \( L \) as time changes from 0 to \( T \), and therefore, \( \xi \) is a function of time (\( \xi = \xi(t) \)). Here, we also define the effective film thicknesses of DLC and stainless steel at \( t = t_0 \) when the instant film thickness is \( \xi_0 = \xi(t_0) \) as follows:

\[
\begin{align*}
  \theta_{\text{DLC}} &= \int_0^{\xi_0} c_{\text{DLC}}(x) dx, \\
  \theta_{\text{SUS}} &= \int_0^{\xi_0} c_{\text{SUS}}(x) dx.
\end{align*}
\]

The meaning of effective film thickness is explained graphically in Figure 4. When the film thickness is \( \xi_0 \), the total amount of DLC inside this graded film is the area below the DLC content profile curve (blue region). If a pure DLC film is made using the same amount of DLC, this film will be represented by the red region in the figure and its thickness is the effective DLC thickness (\( \theta_{\text{DLC}} \)). Note that red and blue regions have the same area.

Now, let us consider only one of the two materials, say \( j \), where \( j \) could be either DLC or stainless steel 316L. Then, we need to develop an scheme for calculating the laser power required for material \( j \) at time \( t_0 \), \( P_j(t_0) \), which can change the content of material \( j \) from \( c_j(\xi(t_0)) = c_j(\xi_0) \) to \( c_j(\xi(t_0 + \Delta t)) \) when it is shined on the target for a time duration of \( \Delta t \). Here, \( c_j(\xi(t_0 + \Delta t)) \) can be approximated by the first two terms of the Taylor series as follows:

\[
c_j(\xi(t_0 + \Delta t)) \approx c_j(\xi(t_0)) + \frac{dc_j(\xi(t))}{dt}_{|t=t_0} \Delta t. \tag{3}
\]

In Eq. (3), the time rate of content change of material \( j \) at \( t = t_0 \) can be calculated using the differentiation rule for a composite function and the chain rule as

\[
\frac{dc_j(\xi(t))}{dt} |_{t_0} = \frac{dc_j}{d\xi} |_{\xi_0} \cdot \frac{d\xi}{dt} |_{t_0} = c_j(\xi_0) \cdot \frac{d\xi}{dt} |_{t_0}.
\]

In Figure 2, the two dissimilar plasma plumes were measured to be 6.17 and 6.57 cm\(^3\)/mol, respectively.

In Figure 3, an ICCD camera image showing the two dissimilar plasma plumes being mixed in space before deposited onto the substrate.

In Figure 4, a schematic diagram of a FGDLC film defined by content profile functions \( c_{\text{DLC}}(x) \) and \( c_{\text{SUS}}(x) \), which are defined on the basis of particle numbers.
Note that if we let \( \int c_j(x) \, dx = C_j(x) \), then \( \theta_j = \int_0^t c_j(x) \, dx = C_j(\xi) - C_j(0) \), and obviously, \( \frac{\partial \theta_j}{\partial \xi} = c_j(\xi) \), or \( \frac{d\theta_j}{dt} = \frac{1}{c_j(\xi)} \). Therefore, Eq. (4) becomes

\[
\frac{dc_j(\xi(t))}{dt} \bigg|_{\theta_j} = c_j(\xi) - c_j(0) \frac{\partial \theta_j}{\partial t} \bigg|_{\theta_j(t)}.
\]

From Eqs. (3) and (5),

\[
\frac{\partial \theta_j}{\partial t} \bigg|_{\theta_j(t)} \approx c_j(\xi) - c_j(\xi(t + \Delta t)) - c_j(\xi(t))
\]

and then Eq. (6) becomes

\[
\frac{\partial \theta_j}{\partial t} \bigg|_{\theta_j(t)} \approx \frac{c_j(\xi)}{\Delta \xi}.
\]

Therefore, our next task is to obtain the laser power that generates \( \frac{\partial \theta_j}{\partial t} \bigg|_{\theta_j(t)} \), or the deposition rate for component \( j \), which needs to be determined experimentally.

In order to obtain deposition rates for DLC and stainless steel 316 L, we have conducted systematic experiments. Figure 6 shows the deposition data of DLC and stainless steel 316 L obtained for several laser power values (1, 2, 3, 4, and 5 W for DLC and 0.25, 0.5, 0.75, and 1 W for stainless steel). During deposition, stainless steel 316 L substrates were used for both materials, and the pressure in stainless steel vacuum chamber was maintained at \( \approx 10^{-5} \) Torr and temperature of substrate was set to 23°C. Targets were rotated at a speed of 80 rpm to minimize the target drilling effect, and the substrate holder was also rotated at 30 rpm for uniformity of deposited film on the substrate. For each laser power and material in Figure 6, the thickness of the deposited film was measured at a 10 min interval up to 60 min. We have also found the deposition threshold powers for the two materials: 0.29 W for DLC and 0.2 W for stainless steel 316 L. In other worlds, below these powers deposition did not take place.

To evaluate the deposition rate, the deposition data in Figure 6 must be expressed mathematically as \( \theta_j(P_j, t) \), where \( P_j \) is the laser power for component \( j \). Note that because Figure 6 was obtained for pure DLC and pure stainless steel, the deposited film thickness is the effective film thickness \( \theta_j \), which is apparently a function of laser power and deposition time (see Figure 6). To obtain the function \( \theta_j \), the deposition data for a given laser power, say \( P_j^* \), was first fitted to the Nelder model, \( \partial \theta_j(P_j, t) = \frac{\theta_j}{b_0 + t/b_1 + t^2/b_2} \), where \( b_0, b_1, \) and \( b_2 \) are the coefficients to be determined. The coefficients \( b_0, b_1, \) and \( b_2 \) for all powers and materials are summarized in Table I, and the fitting functions are shown as lines in Figure 6. Note that because we obtained the deposition data only for a small number of laser powers, in this study, a linear interpolation using neighboring fitting functions was employed for a laser power that was not available in the deposition data. In this way, we obtained \( \theta_j(P_j, t) \) mathematically for any values of \( P_j \) and \( t \) shown in Figure 6.
TABLE I. Coefficients for the Nelder model used to fit the deposition data of DLC and stainless steel 316 L.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.58123</td>
<td>0.001518</td>
<td>1.609 × 10^{-4}</td>
</tr>
<tr>
<td>1</td>
<td>0.2517</td>
<td>0.000407</td>
<td>5.708 × 10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>0.18158</td>
<td>0.000193</td>
<td>3.247 × 10^{-5}</td>
</tr>
<tr>
<td>4</td>
<td>0.14483</td>
<td>0.000137</td>
<td>2.532 × 10^{-5}</td>
</tr>
<tr>
<td>5</td>
<td>0.10051</td>
<td>6.324 × 10^{-5}</td>
<td>9.605 × 10^{-5}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel 316 L</td>
<td>0.25</td>
<td>0.27935</td>
<td>−0.00224</td>
</tr>
<tr>
<td>0.5</td>
<td>0.17646</td>
<td>8.302 × 10^{-4}</td>
<td>8.611 × 10^{-5}</td>
</tr>
<tr>
<td>0.75</td>
<td>0.12576</td>
<td>0.000107</td>
<td>1.511 × 10^{-5}</td>
</tr>
<tr>
<td>1.0</td>
<td>0.07495</td>
<td>−6.077 × 10^{-4}</td>
<td>1.555 × 10^{-5}</td>
</tr>
</tbody>
</table>

Now, the remaining problem is to find a laser power value at time $t_0$ that corresponds to the deposition rate $\frac{\partial \rho}{\partial t} |_{t_0}$, given by Eq. (6) or Eq. (8). Obviously, $\frac{\partial \rho}{\partial t} |_{t_0}$ is a slope of the deposition curve in Figure 6 when the effective film thickness of component $j$ is $\theta_j |_{t_0}$, i.e., $\theta_j |_{t_0}$, and therefore, the corresponding laser power $P_j(t_0)$ can be easily obtained by using linear interpolation. One thing to note here is that at the given effective film thickness of component $j$ ($\theta_j |_{t_0}$) the maximum deposition rate exists, which normally corresponds to the maximum laser power because the laser used to generate the deposition data has a limited power

\[ \frac{\partial \rho_j}{\partial t} |_{\theta_j |_{t_0} \text{max}}. \] (9)

Hence, if a proper laser power does not exist in the range given by Eq. (9), time step $\Delta t$ (i.e., deposition time) must be increased to reduce the required deposition rate accordingly see Eq. (6) or Eq. (8).

III. DEPOSITION OF FGDLC FILMS WITH DESIGNED GRADIENT PROFILES

In this study, as an implementation example, functionally graded DLC films with six different gradient profiles were created: five profiles were defined using the power function and one profile was based on a sinusoidal function. For the five power-function based profiles, films were designed to be 600 nm thick, where the first 450 nm was the gradient region and the outer 150 nm was the pure DLC region. The content profile functions of DLC and stainless steel 316 L are given mathematically as

\[ c_{\text{DLC}}(x) = \begin{cases} \alpha x^n & \text{if } 0 \leq x \leq 450 \text{ nm} \\ 1 & \text{if } 450 \text{ nm} < x \leq 600 \text{ nm} \end{cases}, \] (10)

\[ c_{\text{SUS}}(x) = 1 - c_{\text{DLC}}(x). \]

All six content profile functions for DLC are plotted together in Figure 7.

To build the gradient region, the number of time steps $(n)$ and the deposition time $(T)$ were chosen to be 480 and 60 min, respectively. (Therefore, $\Delta t = 7.5$ s.) The power profiles required to build these content files were calculated using the scheme presented in the previous section and are presented in Figure 8.

After all the films were deposited, the gradient profiles were investigated using the energy-dispersive X-ray spectroscopy (EDS) attached to a scanning electron microscope (SEM, S-4800 Cold Field Emission SEM, Hitachi, Japan). In order to measure the content profile, the EDS analysis was conducted on the side of the deposited film at 16 equally spaced points along the thickness of the film. For a given profile, the measurement was repeated on different deposition samples and an average was calculated. From the EDS measurements, carbon (C) and iron (Fe) contents were studied because carbon is the sole constituent of DLC and stainless steel consists predominantly of iron. Note that while iron is only contained in stainless steel,
both DLC and stainless steel contain carbon. Since stainless steel 316 L contains 59.46% of iron and 6.78% of carbon in terms of atomic composition, the atomic percentages (at. %) of carbon and iron in the film can be broken down as follows:

\[
\begin{align*}
\text{Fe (at. %)} & = \frac{0.5946 \times N_{\text{SUS}}}{N_{\text{total}}} , \\
\text{C (at. %)} & = \frac{0.0678 \times N_{\text{SUS}} + N_{\text{DLC}}}{N_{\text{total}}},
\end{align*}
\]

(12)

where \(N\) denotes the number of atoms. Therefore, the stainless steel and DLC contents can be calculated as

\[
\begin{align*}
c_{\text{SUS}} & = \frac{N_{\text{SUS}}}{N_{\text{total}}} = \frac{1}{0.5946} \text{Fe (at. %)}, \\
c_{\text{DLC}} & = \frac{N_{\text{DLC}}}{N_{\text{total}}} = \text{C (at. %)} - 0.0678 \frac{N_{\text{SUS}}}{N_{\text{total}}},
\end{align*}
\]

(13)

The data points in Figure 9 represent the content profiles of the deposited films calculated by Eq. (13). Solid lines show the content profiles that are originally designed. As clearly shown, for all six cases, the content profiles of the deposited films agree very well with the initially designed content profiles.

In order to quantitatively describe how accurate the deposited film was, we defined the deposition error for component \(j\) as

\[
e_j = \frac{\| \tilde{c}_j(x) - c_j(x) \|}{\| c_j(x) \|},
\]

(14)

where \(\tilde{c}_j(x)\) is the content profile of component \(j\) for the deposited film and \(\| f(x) \| = \sqrt{\int_0^L f(x)^2 dx}\). Because the EDS was taken at 16 equally spaced points along the thickness direction, Eq. (14) can be approximated as
where $\Delta x = L/16$. Calculated deposition errors are summarized in Table III. As shown, the deposition errors for DLC are less than 3% in all cases, and stainless steel has smaller errors, varying between 1.07 and 2.59%. Therefore, we can say that the obtained content profiles agree very well with the original designs.

In this study, we have also measured the film thickness using an alpha-step surface profiler (KLA Tencor P-6). For each sample, thickness was measured 12 times and an average was calculated and summarized in Table IV. Note that films of 600 nm thickness were intended, and the average

![FIG. 9. Content profiles of the deposited films (solid squares and circles) and initially designed content profiles shown as lines.](image)

<table>
<thead>
<tr>
<th>Profile</th>
<th>Average thickness (nm)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>595.6</td>
<td>-0.73</td>
</tr>
<tr>
<td>Quadratic</td>
<td>596.3</td>
<td>-0.62</td>
</tr>
<tr>
<td>Cubic</td>
<td>600.0</td>
<td>+0.01</td>
</tr>
<tr>
<td>Square root</td>
<td>597.4</td>
<td>-0.43</td>
</tr>
<tr>
<td>Cubic root</td>
<td>596.7</td>
<td>-0.55</td>
</tr>
<tr>
<td>Sinusoidal</td>
<td>606.3</td>
<td>+1.04</td>
</tr>
</tbody>
</table>

**TABLE III. Calculated deposition errors of FGDLC films.**

<table>
<thead>
<tr>
<th>Content profile</th>
<th>Error for DLC (%)</th>
<th>Error for stainless steel (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>2.71</td>
<td>1.37</td>
</tr>
<tr>
<td>Quadratic</td>
<td>2.64</td>
<td>1.09</td>
</tr>
<tr>
<td>Cubic</td>
<td>2.99</td>
<td>1.07</td>
</tr>
<tr>
<td>Square root</td>
<td>2.09</td>
<td>1.21</td>
</tr>
<tr>
<td>Cubic root</td>
<td>2.01</td>
<td>1.24</td>
</tr>
<tr>
<td>Sinusoidal</td>
<td>2.32</td>
<td>2.59</td>
</tr>
</tbody>
</table>
measured thicknesses ranged from 595.6 to 606.3 nm. In all cases, the corresponding errors were less than 1.04%, which suggests that the proposed method was very accurate.

IV. CONCLUSION

In this study, we have successfully developed a novel pulsed laser deposition method for fabricating a functionally graded film with a designed gradient profile of any thickness and profile. As an implementation example, FGDLC films with six different gradient profiles have been fabricated successfully, and the thicknesses and content profiles of the deposited films agreed very well with the original designs.

ACKNOWLEDGMENTS

This work was supported by the development program of the local science park funded by the Ulsan Metropolitan City and the Ministry of Education, Science, and Technology of Korea.


