Artificial nacre-like layer using layer coating with bioinspired mesolayer insertions

Pei-Hung Kuo¹ · Ping-Wen Chen¹ · Jenq-Gong Duh¹ Received: 6 September 2019 / Accepted: 11 December 2019 / Published online: 19 December 2019
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Abstract

The fabrication of coatings using conventional methods [e.g., physical vapor deposition (PVD) and/or pulsed laser deposition (PLD)] usually creates clear interfaces between the edges. It is challenging to increase the toughness by adding soft materials into hard materials to reinforce the structures using architectural design. In this study, we determined that by adding soft materials into hard materials, we can simulate nacre, which results in stronger coatings. However, the compatibility of materials needs to be considered (i.e., the bonding of organic/inorganic components to each other). Titanium dioxide (TiO_2), an inorganic material, was chosen as the hard part, and polyimide (PI), an organic material, was chosen as the soft part. When we fused these two materials together to form a layer-by-layer coating, the bonding between them was not good, which degraded the mechanical performance. Nevertheless, we reevaluated the differences between artificial and natural coatings. The layers in nacre smoothly change from chitins to proteins or from proteins to chitins owing to the seasonal environmental temperature changes. Inspired by this concept and by simulating nature, we created mesolayers to adhere two different materials and to enhance the coatings that are made entirely of inorganic or organic materials to create new composites using the PVD/PLD method. The mesolayers mixed with two materials at proper ratios were inserted into the organic/inorganic (PI/ TiO_2) interfaces as bridges to cross-link the materials and dramatically improve the mechanical performance, which is similar to the structure of natural nacre.

Keywords Mesolayer · Bioinspired · PVD · PLD · Multilayers · Coating

1 Introduction

Nature is remarkably adept at using brittle ceramic-like materials as scaffolds for structural applications; the produced materials exhibit excellent strength, toughness, and wear resistance. These characteristics are achieved because of the scaffold structure and soft materials that infiltrate into spaces between the scaffolds to form hierarchical structures. The successful examples include sea shells, pearls, and abalones [1–3]. These materials inspired a new field of composite materials that simulate the abovementioned structures to provide additional bonding and resist the initiation and propagation of cracks [3].

Bioinspired strong materials have been developed using several types of highly technological methods, which reinforce the mechanical performance of these materials. Currently, scientists simulate nature to identify approaches that are required to create functional materials for modern applications [4–15]. Furthermore, structural stability has been enhanced to surpass that of the original materials. Specifically, architectural design is used to manipulate adhesion between layer-by-layer (LBL) interfaces using chemical bath deposition (CBD) [4–9], freeze casting (ice-templating) [10, 13], coextrusion [14] approaches to synthesize periodic coatings, and the physical vapor deposition (PVD)/pulsed laser

✉ Jenq-Gong Duh, jgd@mx.nthu.edu.tw | ¹Department of Materials Science and Engineering, National Tsing Hua University, No. 101, Section 2, Kuang-Fu Road, Hsinchu 30013, Taiwan.

deposition (PLD) method [15] is used to form LBL/lamellar structures in a high vacuum system. Using CBD and freeze casting methods, it is possible to create a “brick and mortar” structure that is very similar to that of natural nacre. The PVD/PLD method can only create an LBL structure, and it is a nearly pure physical process without sufficient chemical reactions to create bonding; chemical reactions are possible only in a short range close to the interface. However, the deposition can be well controlled and produce structures with structures that are 1000 nm thick. Yang et al. have successfully deposited zirconia (an inorganic part) by reactive RF sputtering and polyimide (an organic part) by a pulsed laser deposition system. A multilayered structural hybrid coating was achieved; its fracture toughness exceeded that of the original materials, which implies that the new composites could absorb more energy [15].

In this study, owing to their thermal and chemical stabilities and non-toxic characteristics, titania (a cheap, chemically stable, and widely used material) was chosen as an inorganic part, and a polyimide (PI) nanofilm was used as an organic part to construct nacre-like LBL coatings [16, 17]. However, the addition of TiO_2 may cause reduced elongation of the nanocomposite film, which acts as a non-reactive, non-reinforcing filler if there are no bonding sites between PI/ TiO_2 [17]. Previous studies evaluated the compatibility of the physical processes to make sure that complete infiltration without unexpected effects occurred; these studies applied additional post-treatments (e.g., quenching or sintering) to increase bonding [13, 14].

To overcome the disadvantages from the poor compatibility of PI/ TiO_2 , we implemented two improvements. The first improvement is to increase the repetition of coatings. According to the research by Burghard et al. [6, 7], the bonding between the interface of PE/ TiO_2 (organic/inorganic) is needed to reduce the thickness of the organic layer to allow partial interpenetration to form regions with a mixed composition that are promoted by electrostatic attractions. The second improvement is to create a mixed layer with its organic/inorganic part and insert it into the interface between these two materials without a reliable bonding. By observing the growth of nacre, it was determined that the growth of chitins or proteins does not considerably differ from one to another, and a smooth crossover occurs to form a transition area called mesolayer; this process follows the seasonal changes in temperature. [18–22].

Based on these two concepts, a mixed organic/inorganic mesolayer with a suitable ratio has been introduced to the interface between PI/ TiO_2 to improve the adhesion. The thickness of PI/ TiO_2 is reduced to induce higher interpenetration in the PI films. More repetitions can be achieved to enhance the compressive stored energy.

2 Materials and methods

Pre-cleaned p-type silicon wafers with a $\langle 100 \rangle$ orientation were ultrasonically cleaned in DI water, rinsed with a 95% alcohol, and dried. Subsequent to this procedure, the substrates were ready for deposition. A pure titanium target (99.99%, Ultimate Materials Technology Co., Ltd., Hsinchu, Taiwan) with a diameter of 5.08 cm (2 inches) was utilized to deposit a titania film by reactive magnetic sputtering in an argon and oxygen atmosphere. In this study, a polyimide (PI) target was used to deposit polymer interlayers. A polyimide bar (Ultimate Materials Technology Co., Ltd., Hsinchu, Taiwan) [30 cm long with a diameter of 2.54 cm (1 inch)] was evenly sliced into 10 polyimide targets with thicknesses of 3 cm. The exposed surface of the target was flattened and polished by sandpapers and alumina powders.

The hybrid PVD system, which included sputtering and PLD, was designed and integrated in the same vacuum chamber. Two coating systems can be operated within one vacuum chamber sequentially or cooperatively using pre-determined procedures.

The substrate was attached to the substrate holder. The holder is continuously rotated during the sputter and/or PLD processes. In addition, during the PLD procedure, the PI target moved horizontally back and forth to allow the laser spot to irradiate the entire target to minimize the formation of trenches owing to the laser etching phenomenon and to ensure a uniformly vaporized organic film deposited onto the surface of the substrate. The organic film was deposited by the Nd:YAG laser source with built-in harmonics (LS-2137U, Lotis TII Corporation, USA). The wavelength of the UV-pulsed laser was 266 nm, and the energy was set to 30 mJ. The argon atmosphere was introduced into the chamber during the PLD process to induce localized plasma to increase the surface roughness of polymer films. TiO_2 /PI multilayer coatings were synthesized by sequentially using sputtering and PLD. The TiO_2 /PI ratio was kept at 10:1. Four groups of multilayer coatings with varying periodic thicknesses (in nm) of TiO_2 /PI were fabricated: 100/10, 75/7.5, 100/10 with a mesolayer, 75/7.5 with a mesolayer, and 50/5 with a mesolayer (Fig. 1). The total thickness of the multilayer films was approximately 1000 nm. In addition, titania and polyimide monolayer films were fabricated by sequentially manipulating PVD and PLD. The mesolayers were fabricated by cooperatively using PVD and PLD with suitable parameters. Table 1 shows the conditions and parameters used in this study.

The phases were identified by a grazing incidence X-ray diffractometer (GIXRD, TTRAX III, Rigaku, Japan) using a Cu-K α radiation operated at 50 kV and 300 mA.

Table 1 Design of nacre-like LBL hybrid coatings

Code	Thickness (nm)			TiO ₂ /PI ratio in the mesolayer	Repetition	Total Thickness (nm)
	TiO ₂	Mesolayer	PI			
TPI 100	100	–	10	–	10	Approx. 1000 nm
TPI 75	75	–	7.5	–	12	Approx. 1000 nm
TPI 100 Mso	100	1.5	7	5/1	10	Approx. 1000 nm
TPI 75 Mso	75	1.5	4.5	5/1	12	Approx. 1000 nm
TPI 50 Mso	50	1.5	2	5/1	18	Approx. 1000 nm

Fig. 1 Schematic diagram of the layer structure (TPI 50 Mso) for mesolayer insertion

The chemical composition of the thin film was analyzed by a field emission electron probe micro-analyzer. (FE-EPMA, JXA-8500F, JOEL, Japan). The morphology and microstructure were observed by field-emission SEM (JSM-7600F, JEOL, Japan). The intrinsic mechanical properties of the coatings were measured by a nanoindenter (NHT, CSM instrument) under a 5-mN maximum test load. A loading of 100 mN was applied to induce cracks to determine fracture toughness. Moreover, the adhesive strength was evaluated by a scratch test in a scratch mode. All TEM samples were prepared by a focused ion beam system (FIB, Helios Nanolab 600i, The FEI Company, USA). The microstructure of the multilayered structure was observed by high-resolution transmission electron microscopy (HR-TEM, JEM-3000, JEOL, Japan).

3 Results

Based on the architectural design shown in Table 1, two groups of comparable results can be identified. The one is conventional LBL coatings stacked by TiO₂ and PI sequentially by physical deposition methods, and the other one is according to the original LBL coatings and insert mesolayers that were implied between PI and TiO₂ interfaces. To

understand the effects of repetitions and mesolayer insertions, mechanical properties were evaluated because they are the most important indices.

The results of hardness and elastic modulus are shown in Fig. 2. Hardness increased with additional repetitions, even without the insertion of mesolayers. In contrast, modulus only increased with an increase in the number of normal LBL hybrid coatings, yet decreased with an increase in the number of coatings with mesolayers in between the TiO₂/PI interface. This means that the energy was transferred much farther and more layers were linked to transform the brittle tendency to extendable one. This indicates that the modified hybrid coatings can withstand more energy, i.e., the coatings became stronger and more flexible, which helps to reinforce the structural stability. This shows that the LBL structure exhibits stronger architectural performance than the two raw materials individually.

Figure 3 shows the calculated values of H/E (i.e., the combined index of hardness and modulus). Compared to the studies of Burghard et al. [6, 7], a TiO₂/PE LBL system with the same ratio of 100 nm/10 nm (TPE 100) was also analyzed. In the beginning, the H/E ratio of TiO₂/PI exhibited poor performance, even weaker than the original TiO₂ coating. Unlike the results of TPE 100, the

Fig. 2 Hardness and elastic modulus of LBL hybrid coatings measured by nanoindentation

Fig. 3 H/E ratio of LBL hybrid coatings

reinforced LBL structures of the TiO_2/PE system are achieved by CBD. However, the H/E ratio increased with the insertion of mesolayers into the TPI system. The H/E ratio of TPI 100 Mso was approximately equal to that of the original TiO_2 coating and surpassed that of TPE 100 when the thickness of each interlayer decreased and the number of layers increased. The H/E value of TPI 50 Mso was approximately 15–17% higher than that of the TPE 100 hybrid coating system.

To characterize the improvement in adhesion between TiO_2 and PI, fracture toughness was also measured and calculated by:

$$K_{1C} = \alpha \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{C^{3/2}} \right) \quad (1)$$

By calculating fracture toughness, it was determined that the values of the LBL coating with mesolayer insertions were higher than those of the original LBL coating and pure TiO_2 and PI coatings.

Figure 4 shows the trends compared to H/E values. Fractural toughness improved by periodically decreasing the thickness and inserting mesolayers. The K_{1C} value considerably increased when the mesolayers were added, and the value was higher than that of the TiO_2/PE system

Fig. 4 Calculated fractural toughness of LBL coatings compared with those of pure TiO_2 and TPE 100

[6, 7]. Specifically, TPI 100 Mso and TPI 75 Mso were twice as strong as the original TPI 100 and TPI 75, respectively. In addition, the energy absorbability of TPI 50 Mso was greater than that of TPE 100 by approximately 40%.

By performing a corresponding scratch test, it was determined that the propagated cracks were suppressed and a greater adhesion was achieved between TiO_2 and PI. Figure 5a further confirms the abovementioned observation. Before the indentation tip penetrated into LBL coatings, unwanted cracks were revealed. It is argued that the brittle ceramics (i.e., TiO_2) cannot absorb too much energy without the assistance from the soft material, PI. It appears that TiO_2 did not adhere well to PI and behaved as a single material. A comparatively stronger scheme is shown in Fig. 5b. Specifically, compressive force can stop the propagation of cracks, and no significant cracks appear during the scratch test. Even when the tip touched the surface of

the Si wafer, the coating remained intact. Nevertheless, LBL coatings can store more energy with an increase in the number of layers with the same total thickness without inserting mesolayer coatings, i.e., fracture toughness can be slightly increased. After inserting mesolayers as bridges to connect TiO_2 and PI, we can improve the adhesion between TiO_2 and PI (Figs. 4 and 5). The quantitative value of adhesion can be determined by calculating crack propagation resistance (CPR) to determine the effect of mesolayer insertions using the equation shown below:

$$\text{CPRs} = \text{LC1} (\text{LC2} - \text{LC1}) \quad (2)$$

The calculated values are shown in Fig. 6. The resistance values were lower than those of pure PI and TiO_2 without mesolayers. Thus, the combination of harder material and softer material to produce a new

Fig. 5 SEM observation of scratch tests for **a** TPI 75 and **b** TPI 75 Mso

Fig. 6 Calculated crack propagation resistance of LBL coatings compared with those of pure TiO_2 and TPE 100

composited LBL coating did not exhibit a positive phenomenon. Subsequent to inserting a mesolayer between TiO_2 and PI by sputtering and PLD co-deposition, the system could withstand and absorb more

energy owing to the contribution of mesolayers, which bonded these two materials by weak bonding. To explore the created bridges in detail, HR-TEM observations were performed. Figure 7 clearly shows that the

Fig. 7 HR-TEM observation of PI/Meso structures for **a** TPI 100 and **b** TPI 50 Mso

structure was accurately controlled by the designed parameters. By comparing Fig. 7a and Fig. 7b1, it is determined that the original PI acted as a wall that separated TiO_2 into two parts. Unlike the PI + meso structure, there were two meshes or small webs that linked and connected TiO_2 to form a transition. Moreover, there were no significant sharp zones in the transition areas shown in Fig. 7b2. The transition areas were formed and provided a smooth crossover path for energy dissipation and additional bonding between inorganic and organic parts. In this study, two promising materials were chosen to form an LBL coating inspired by nacre. However, favorable results were not obtained using a structure similar to nacre if the two materials did not have sufficient bonding. Thus, mesolayers were added to force TiO_2 and PI to bond by web-like interconnections. The best results were obtained by depositing more layers and inserting mesolayers between these layers, i.e., TPI 50 Mso. This structure can absorb approximately 50% more energy than that of pure TiO_2 coating, and the ability to prevent cracks is 70% better than that of pure PI. The H/E ratio, fracture toughness, and CPRs values reach or surpass those of TPE 100 [6, 7], as demonstrated by TPI 75 Mso and TPI 50 Mso.

4 Discussion

As seen in Fig. 2, the hardness of the system elevates as a result of more repetition, whereas the elastic modulus only increases with repeated additions of conventional LBL coatings via physical deposition methods. On the other hand, the elastic modulus decreases with more repetitions during the insertion of mesolayers into the TiO_2 and PI interfaces. This means that a toughened film can be mimicked since the strain that is exerted increased when stress is applied; in other words, deformation of the system becomes larger before the appropriate yield stress level is reached. The benefit of this is that, in the event of subsequent system failure, the LBL coatings are less brittle when compared to their original mechanical performance. In Fig. 8a1, it could be seen that the LBL coatings delaminated from the interfaces between TiO_2 and PI after bending. The TEM samples shown in Figs. 8a2, b2 were prepared using focus ion beam methodology (FIB). The stress applied during experimentation procedures was very small and, thus, could be ignored. Whereas evidence of the delamination phenomena could be clearly observed in the TEM images (Fig. 8a2), there was no delamination to be seen during insertion of the mesolayers (Fig. 8b1, b2). The results from our experiments are, thus, concluded as the H/E ratio, which is used to compare the combined

Fig. 8 A comparison of SEM images for **a1** the original LBL TiO_2 /PI coatings (TPI 100) and **b1** LBL TiO_2 /PI coatings with the mesolayers inserted (TPI 100 Mso). TEM images for **a2** the original LBL TiO_2 /PI coatings (TPI 100) and **b2** the LBL TiO_2 /PI coatings with the mesolayers inserted (TPI 100 Mso)

effects of hardness and elastic modulus (Fig. 3). The H/E ratio reflects the mechanical properties of the system and highlighted the novelty of the LBL coatings during mesolayer insertion. The TPI 100 Mso values for the hardest sample from the raw materials investigated in our study are similar to those of the original TiO_2 coatings and can be further increased with more repetition (TPI 75 Mso and TPI 50 Mso). Finally, the values obtained for the LBL coatings that have been applied via physical processes with the respective mesolayers inserted (TPI 50 Mso) surpassed those for the TiO_2/PE system that had been prepared via CBD (TPE 100).

To prove that the LBL coatings with mesolayers can be subjected to much higher energy input, the TiO_2/PI interfaces are first reinforced; during this process, it is revealed that the coatings exhibited better adhesion (Fig. 8). Next, quantitative tests are conducted via the scratch test and the nanoindentation methods. From Fig. 5a, it can be seen that extensive cracks propagated from the edges of the scar radially and perpendicular to the scratch's direction. This highlights the inherent weakness of the LBL coating since bonding between the interfaces is insufficient and cannot stop the formation of cracks. Similar results are also seen in Figs. 4 and 6. Indices related to the coating's ability to stop the propagation of cracks can be identified using the CPRs and K_{1C} values. If adhesion of the interfaces is poor, then the cracks' tip can propagate and spread through interfaces with lower barriers, thus dissipating the energy input that has been applied to the system. Since both the soft and tough materials, i.e., the organic portions (PI), cannot act as a means of stopping the propagation of cracks during the application of energy to the brittle portion of the system, i.e., the inorganic part (TiO_2), the path taken by the cracks extended from the surface of TiO_2 and the TiO_2/PI interfaces. In contrast, Fig. 5b shows that the PI portion hinders the propagation of cracks, since the path of propagation does not appear on the surface and a closed-loop oval can be seen surrounding each scratch. As exemplified by the results shown in Figs. 4 and 6, the process of propagation is constrained and can be subjected to higher energy input.

It is also worth noting how the type of material used in our experiments influenced the outcome. PI is a thermosetting plastic, whereas PE is a thermoplastic polymer.

Generally, thermosetting plastic materials exhibit sturdier mechanical properties and better thermal stability. The H/E values for PI shown in Table 2 demonstrate that PI exerted more influence on the toughness of the LBL coatings. Comparing the physical properties of both PI and PE, it can be seen that PI has a significantly higher melting point which translates to the preservation of its function even at higher temperatures. Thus, in light of these add benefits, i.e., the H/E value and higher stability, more modern systems that mimic LBL films can be achieved via physical sputtering and PLD methods. Unfortunately, the results of the mechanical tests conducted are unexpected and show the presence of delamination. In the SEM images (Fig. 8a), poor adhesion is noted to be the root cause of these terrible performances. As shown in Fig. 6, after the introduction of mesolayers mixed with TiO_2 and PI in the proper ratio and insertion into the interfaces between TiO_2 and PI, the CPRs values are compatible with TPE 100 in same architectural design (TPI 100 Mso). Furthermore, the fractural toughness of TPI 100 Mso is higher than that seen in the TPE system. This is quite an important advancement in creating the appropriate bonding interactions between TiO_2 and PI.

In Fig. 9, the schematic model that is derived by carefully observing the TEM images (Fig. 7b1) is presented. Herein, PI is shown to be stretched inside the mesolayers that are cross-linked to form a web-like interlace which helps with adhesion of the PI layers, while the mesolayer still maintains the characteristics of TiO_2 bonded with the pure TiO_2 layer. The mesolayer, as a transient zone, is connected with TiO_2 and PI together using physical deposition methods to insert the TiO_2/PI interfaces in the correct ratio in order to simulate natural growth mechanisms.

5 Conclusion

By inserting mesolayers into original coatings of the TiO_2 and PI LBL architectural design, we solved the problem of poor adhesion between TiO_2 and PI. Mixed composites can be created by simultaneously performing sputtering and LPD using a lower sputtering rate and a higher LPD rate to achieve desired compositions. In this study, the mechanical performance of the produced films can exceed those

Table 2 Comparison of the candidate materials

Materials	Mechanical properties			Physical properties		
	Hardness (GPa)	Elastic modulus (GPa)	H/E	Cross-linking type	Melting point (°C)	CTE (ppm)
TiO_2	1.72	27.7	0.062	NA	1843	10
PE	0.45	5.0	0.090	Thermoplastic	115	110
PI	0.25	2.2	0.113	Thermosetting	375	90

Fig. 9 Schematic mechanism for showing the correlation between the mesolayer/PI and mesolayer/TiO₂ interfaces

of the original individual coatings and TiO₂/PE system by increasing the number of layers. By adding mesolayers and increasing the number of layers with the same thickness, LBL coatings can be produced regardless of the chemical compatibility of materials. This approach mimics nature. Specifically, with the seasonal fluctuations in temperature, the creatures respond by forming a composite material in the transition stage. Thus, using a similar approach, a composite material (i.e., mesolayer) is created to mimic nature.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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