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LETTER

# Reduction of large particles in the fibroin thin films prepared from near-IR pulsed laser deposition by target consolidation

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In our previous studies on the pulsed laser deposition (PLD) of fibroin by near IR beam, we stated that PLD enables us to prepare nanostructured thin film without damaging proteinous secondary structure [1]. We also reported existence and significance of the smallest protein units (SPUs) below 50 nm, in the protein films prepared either via a colloidal route [2] or via physical vapor deposition like PLD [1, 3].

We paid efforts to homogenize the PLD film by choosing appropriate substrate, for the former [2], and to reduce the energy density and select appropriate background gas conditions for the latter [3]. Deposition of structural units much larger than SPU, i.e. debris or droplets during operation is a serious drawback of PLD procedure, together with its low rate of deposition. While we proposed to reduce these chunks by post-treatments [4], we have yet to reduce or avoid formation of large particles in a deposited film.

We suspect that particle pullout from the target is one of the main reasons for debris formation [4]. We therefore examined in the present note the effect of binder for better consolidation of the ablation targets, in an attempt to avoid or reduce the amount of debris and to obtain smoother and more homogeneous nanostructured fibroin films.

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For better consolidation, we granulated SF powders (Idemitsu Petrochrmical Inc. with $\beta$-sheet structure, average particle size 7.9 μm) by extrusion via a sieve mesh of 840 μm opening after adding hydroxylpropyl methylcellulose (HPMC; Shinetsu Chemicals, Metlose 60SH-15) up to 10 wt% and 10 ml of water to serve as a binder. After drying the granules in air at 50 °C for 12 h, they were confined in the cylindrical mold of 30 mm diameter and compressed at 100 MPa for 5 min to obtain the targets SFH$n$, where $n$ denotes the weight percent of HPMC. Deposition was performed on Si (100) wafer (Komatsu Electronic Metals, p-type, Br doped) by using Nara Laser Ablation System (Nara Machinery), equipped with 1064 nm Nd:YAG laser, pulse width of 5 ns, and pulse frequency of 10 Hz. Details of PLD procedure are given elsewhere [1].

Microstructure and surface morphology of the film were observed under a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi) and an atomic force microscope (AFM, SPM-9500J3, Shimadzu and Nanoscope IV, Veeco). Obtained SEM images were corrected by using a photo-retouch software Adobe Photoshop® to gain the best contrast to capture debris particulates. The images before photo-retouch are shown in Fig. 1a and b, and after correction in Fig. 1c and d. Particle size distributions and amount of debris in the films were quantified from the image analysis using a software, Image J® (Image-Pro discovery, The Enhanced Solution For Image Analysis). The debris in the deposited film is to be defined on the area basis. We therefore defined percent area of debris, $A_d$, as the projected area occupied by particles larger than 2.4 μm, recognized by scanning electron micrographs like Fig. 1c and d with twice of the resolution limit, 1.2 μm/pixel. To obtain volume based concentration of debris, we have to

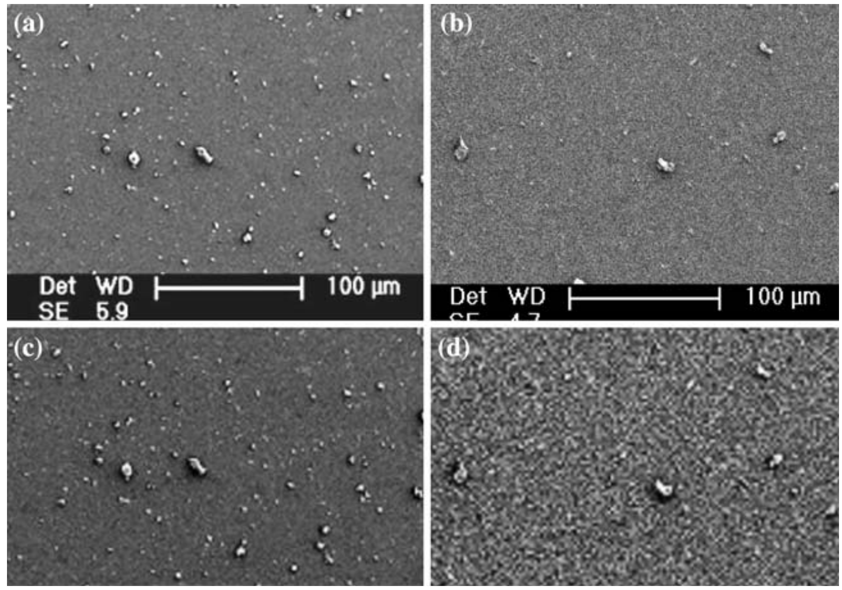


**Fig. 1** SEM images of (**a**, **c**) SFH0, (**b**, **d**) SFH10 films deposited by PLD at 5 J/cm$^2$ for 2 min. (**c**–**d**) images are photo-retouched data of (**a**–**b**)

know 3-D structure of the deposited film, which is out of the scope of the present study.

The film thickness was evaluated by a quartz crystal microbalance (QCM, CRTM-6000, ULVAC). The values of the weight of the deposits, directly monitored by QCM, was converted to the thickness by adopting the average apparent density determined by measurement of a diameter, thickness, and weight of the target of SF, 1.1 g/cm$^3$. Micro Vickers hardness of the target was determined by using a conventional tester (Akashi, MVK-F II) by averaging the size of the 10 indents within an area of $20 \times 20$ mm$^2$ at a minimum distance between indents 3 mm on the target.

From SEM images as shown in Fig. 1, we evaluated the percent debris $A_d$. As shown in Table 1, $A_d$ decreased significantly with increasing the concentration of HPMC, i.e., to one half of the value without a binder by adding 10% HPMC. In contrast, the average particle sizes of SPU, acquired from AFM images shown in Fig. 2, was 23.8 nm without HPMC and apparently decreased to 23.1 nm by adding 10% HPMC. However, the apparent change cannot be significant since the resolution of the image is 4 nm/pixel. It is important to note however, that the variation coefficient of the SPU particle size decreased by a factor 3–4 by the addition of the binder. Thus, the results of Fig. 1 and 2 unequivocally demonstrate that the use of binder brings about more uniform film, including its nanostructure. We did not observe any significant and systematic change in the deposition rate as a function of HPMC concentration, particularly at the first few minutes, being 10 ± 2 nm/min. We therefore conclude that the presence of HPMC reduces debris and reduces the fluctuation of SPU sizes without significantly affect the deposition rate.

The intact target without HPMC comprises densely packed SF powders, as shown in Fig. 3a. We actually observe the traces of the pullout of particles in the target after irradiation as shown in Fig. 3 b by arrows. On the other hand, by adding 5% of HPMC, the gap between SF particle of the target narrowers as shown in Fig. 3c, and the direct pullout from the surface also decreased after irradiation, as shown in Fig. 3d. The micro Vickers hardness increases with increasing the HPMC concentration in the binder, as also shown in Table 1. Simultaneously, the variation coefficient of the micro Vickers hardness was decreased, implying the increase in the homogeneity of the target as well. $A_d$ value decreases almost linearly with $R^2$ = 0.9997

**Table 1** Average size of nanoparticles, coating rate of debris of the films, and Vickers hardness of the SF targets prepared by different binders

| | | SFH0 | SFH 5 | SFH 10 |
|---|---|---|---|---|
| Average size ofnanoparticles | By A FM [nm] | 25.8 ± 3.2 | 22.2 ± 0.7 | 23.1 ± 1.0 |
| | Variation coefficient [-] | 0.12 | 0.03 | 0.04 |
| | By SEM [nm ] | 23.8 | 21.1 | 23.0 |
| Percent area of debris | $A_d$ [%] | 2.5 | 1.6 | 1.3 |
| Vickers hardness of the target | [–] | 44.4 ± 20.4 | 86.3 ± 29.3 | 101.5 ± 18.9 |
| | Variation coefficient [–] | 0.46 | 0.34 | 0.18 |

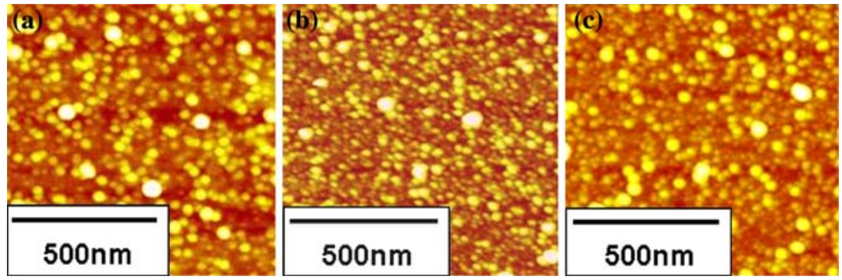


**Fig. 2** AFM images of (**a**) SFH0, (**b**) SFH5 and (**c**) SFH10 films deposited by PLD at 5 J/cm$^2$ for 2 min

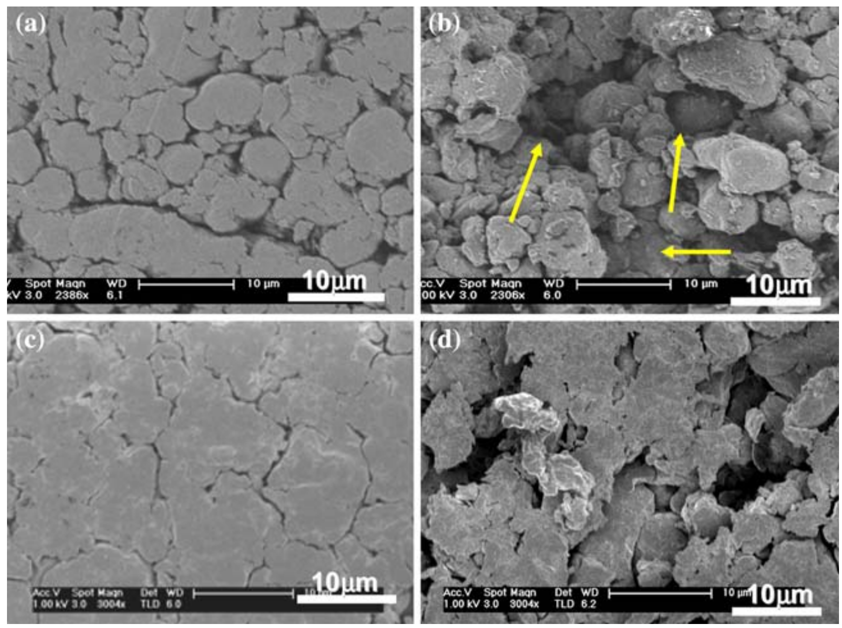


**Fig. 3** SEM images of (**a–b**) SFH0 and (**c–d**) SFH5 target (**a**, **c**) before and (**b**, **d**) after irradiation of 1064 nm laser at 5 J/cm$^2$

with increasing the micro Vickers hardness, as shown in Fig. 4. This is straightforwardly associated with the decrease in $A_d$ by suppressing the pullout of the SF particles right from the target. However, simultaneous change in the nanostructure, the increase in the homogeneity of SPU in particular, cannot be a direct consequence of increase in the interparticle cohesion. Here, homogenization of the film by the introduction of binder should be interpreted in the light of more detailed mechanisms of the deposition.

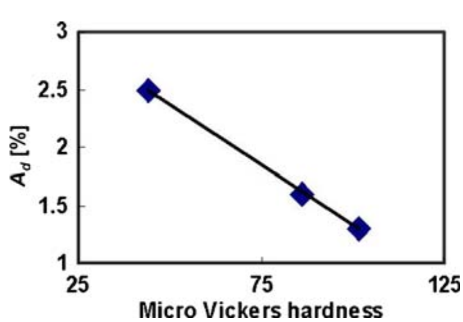


**Fig. 4** Relation between micro Vickers hardness of the target and $A_d$ of the film

As we mentioned in our previous reports [1, 3], the deposition mechanism of the present PLD of fibroin, which is transparent to 1064 nm near IR beam, is associated with a kind of optical breakdown and consequent ionization and local plasma formation [5]. Relative chance of fragmentation within each SF particle in the target due to optical breakdown must be larger than those at the grain boundary when the interparticle adhesion is stronger and hence the relative probability of the fragmentation along the interparticulate boundary decreases due to stronger adhesion with increasing the HPMC concentration. Another factor is a decrease of surface asperity of the target surface by HPMC binder, as non-uniform surface is known to induce irregular optical breakdown [6]. Farther evidence of the mechanism of ablation, including the effect of improvement of the nanostructures is needed for definite mechanism of film homogeination.

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