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Boron nitride fibers were found to grow on polycrystalline nickel and Si(100) substrates by plasma-assisted laser chemical vapor deposition from $B_2H_6+NH_3$ using an excimer laser at 193 nm. Their diameter was typically a few hundreds of nanometers, while the length was a few tens of micrometers. They were stoichiometric or boron-rich BN in chemical composition. When the substrate was rotated during deposition, spiral fibers were found to grow. We conclude that they grew with the help of laser light by other than the vapor - liquid - solid mechanism. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2188381]

We reported previously that sp^3-bonded BN microcones grew by plasma-assisted laser chemical vapor deposition (PAL-CVD) from $B_2H_6+NH_3$ diluted in Ar, using ArF 193 nm laser.[1] The surface of those films was covered by cone-shaped units of about 10 μm in length, and they showed excellent electron field emission properties.[1] They unidirectionally grow toward the laser light by photochemically activated processes, similar to those previously found for the deposition of boron.[2] Here we report the growth of fibrous BN by the same PAL-CVD method under slightly different conditions.

The samples were prepared by PAL-CVD, in almost the same manner as reported previously.[1,3] The source gases were fed at a rate of 2.5 SCCM diborane (B_2H_6), 10 SCCM ammonia, and diluted in Ar(3000 SCCM) for a total chamber pressure of 10 Torr. A Si(100) or polycrystalline Ni disk 2.5 cm in diameter and 0.5 mm thick was employed as the substrate. The substrate temperature was kept at 850 °C during deposition. From the source gases an inductively coupled plasma (ICP), with an electric power of 200 W and a frequency of 15 MHz, was generated at the top of a reaction chamber and directed downward across the surface of the substrate. In our previous experiments, the substrate was inclined 45° to the plasma flow.[1] While the laser irradiated portion of the film always shows excellent adhesion, to avoid peeling from the unirradiated areas on Ni substrates it was found necessary to predeposit a boron buffer layer. Boron was deposited by plasma-assisted CVD under the same conditions as the sample preparation minus the ammonia gas and laser irradiation. The predeposition was not carried out when Si(100) substrates were employed.

A 193 nm ArF excimer laser with a pulse width of 20 ns was introduced horizontally into the reaction chamber, and incident normal to the substrate surface over the rectangular area of 5×11 mm^2. The laser operated at a repetition rate of 10 or 20 Hz with the pulse energy of 175 mJ. The ICP was modulated with a square-wave signal at 10 Hz, and was synchronized with the laser pulse. As a result, the modulated plasma was ejected as repetitive plasma packets down across the substrate while the synchronously pulsed laser hits the substrate surface simultaneously in order to stimulate some (at present unknown) synergetic effects during the deposition.

We employed three modes for the relationship between the modulation signal of the plasma and the laser pulses. The modulation of the plasma by a square-wave signal was fixed at 10 Hz, while the repetition rate of the laser pulsation was 10 Hz in modes A and B and 20 Hz in mode C. The delay of the laser pulse from the beginning of the modulation signal was 30 and 80 msec in modes A and B, respectively. In mode C, the laser pulses were on with delays of 30 and 80 msec after the beginning of the modulation signal. It is shown in

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TABLE I. Summary of the experimental results.

Sample	Substrate	Deposition time (min)	Mode	Substrate rotation (rpm)	Fiber growth	Figure
Ni-10-B	Ni	10	B	···	yes	Fig. 1
Ni-10-C	Ni	10	C	···	yes	
Ni-30-C	Ni	30	C	···	yes	
Ni-30-B1	Ni	30	B	···	yes	
Ni-55-B	Ni	55	B	···	yes	
Ni-90-C	Ni	90	C	···	yes	
Si-26-C	Si (100)	26	C	1	yes	
Si-45-C	Si (100)	45	C	1	yes	Figs. 2 and 3
Ni-10-A	Ni	10	A	···	no	
Ni-20-A	Ni	20	A	···	no	
Ni-30-A	Ni	30	A	···	no	
Ni-60-A1	Ni	60	A	···	no	
Ni-60-A2	Ni	60	A	···	no	
Ni-90-A	Ni	90	A	···	no	
Ni-120-A	Ni	120	A	···	no	
Ni-93-B	Ni	93	B	···	no	
Ni-30-B2	Ni	30	B	···	no	
Ni-120-B	Ni	120	B	···	no	
Ni-60-B	Ni	60	B	···	no	
Ni-120-B	Ni	120	B	0.5	no	

Table I that no fibrous growth was found in the case of mode A. This is likely related to the fact that plasma packets arrive at the substrate a few tens of milliseconds after its generation in the plasma torch, as indicated by our preliminary measurements of the plasma flow rate by using two photodiode probes. Then, the chemical or charged species generated in the plasma packets are considered to be responsible for the fibrous growth of BN.

The morphology and chemical composition of samples were examined with scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS), respectively. The excitation of x ray for the EDS was achieved at an acceleration energy of 20 kV.

On the major rectangular part on the substrate, corresponding to the distribution of the laser intensity, the growth of sp^3-bonded 5H-BN cones were found as reported previously.[1] On the other hand, in the peripheral region around the major rectangular part within 2 mm distance, in the tails of the Gaussian distribution of the laser intensity, microfibers were found to grow. The results are summarized in Table I. It should be noted that no fibrous BN was found to grow by plasma CVD only, without laser irradiation under corresponding conditions, indicating that the ultraviolet laser irradiation at 193 nm is needed in the fibrous growth of BN. It is also known from this that the fibrous growth is dependent on the laser intensity (that is, the surface photon density). The higher photon density in the major rectangular part yielded the cone formation while the lower photon density in the peripheral region resulted in the fibrous growth. The threshold of the surface photon density for this morphological transition remains to be found.

From the overview of the fiber growth it was seen that the diameter of the fibers was uniformly about 1 μm, while the length varied from a few micrometers to 10 μm. A tendency toward a uniform diameter in the samples is seen in all of these experiments.

Detailed views of a fiber found in the sample Ni-10-B is shown in Fig. 1. The overview, tip, middle, and root part of the fiber are shown in Figs. 1(a)–1(d), respectively. The dotted rectangles drawn in Figs. 1(b)–1(d) correspond to the selected areas for EDS measurements as shown in Fig. 3. The diameter is almost constant throughout the fiber, which also was seen as a general tendency in these experiments. The fiber shows a scaly surface, indicating a polycrystalline texture on the surface. However, it is not known yet if this appearance excludes such a coaxial or highly ordered structures as found in multiwall carbon nanotubes.[4,5] The size of the surface scales are about 50 nm. The tip has a hemispherical shape. In the middle part, a small bump and a kink with about 20° are seen. The root has a slightly bulbous shape as is seen in Fig. 1(d). The crystal structure of the fibers remains to be examined and we plan to carry out cross-sectional transmission electron microscopy. Based on our past experimental results, where the low-intensity of laser around the major square part yielded sp^2-bonded BN, it is empirically expected that the fibers are made of sp^2-bonded BN.

Figure 2 shows fibers found in the sample Si-45-C, which was prepared on a Si(100) substrate for 45 min with the pulse mode of type C. In this case, the substrate was rotated with the rotation axis normal to the center of the

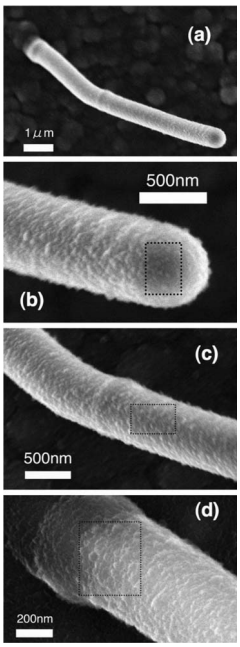

FIG. 1. Detailed views of a fiber found in the sample Ni-10-B.

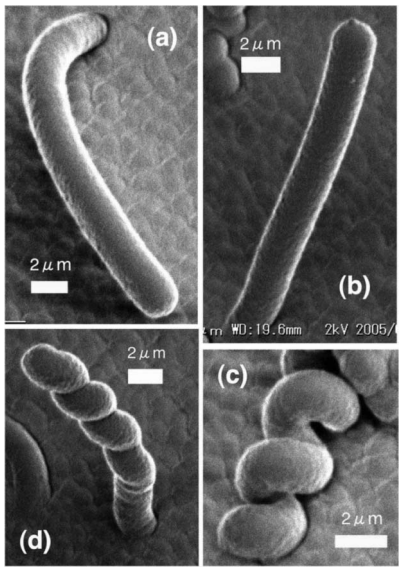

FIG. 2. Fibers found in the sample Si-45-C. In this case, the substrate was rotated with the rotation axis normal to the center of the substrate disk at 1 rotation per minute.

substrate disk at 1 rotation per minute (rpm). The diameters of the fibers are uniformly about 2 μm in this sample and are constant throughout the length of a fiber. The fiber in Fig. 2(a) is slowly curving while that in Fig. 2(b) is almost straight. The most interesting thing with this sample is the spiral-shaped fibers as seen in Figs. 2(c) and 2(d). The spiral growth of fibers requires the rotation of the substrate, probably because the directional growth is activated photochemically and follows the rotation of local intensity of the laser on the fiber tip. Further investigations are needed to clarify the growth mechanism of the spiral fibers.

In Figs. 3(a) and 3(b), the EDS spectra from the samples Si-45-C and Ni-10-B are shown, respectively. In Fig. 3(a), the inset shows a SEM image of the examined area. The chemical composition estimated from the spectrum in Fig. 3(a) was B:N:O=45.5:44:10.5 (at. %) using standard sensitivity coefficients. We may understand that the signals from O and C are from the surface contamination, and the sample

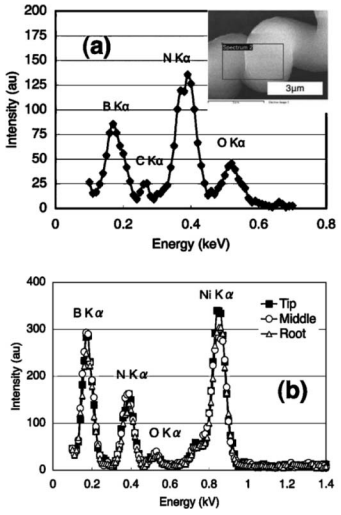

FIG. 3. (a) and (b) show the EDS spectra from the samples Si-45-C and Ni-10-B, respectively. (b), The EDS spectra corresponding to Fig. 1 are plotted.

Si-45-10 is almost stoichiometric in chemical composition.

In Fig. 3(b), the EDS spectra corresponding to Fig. 1 are plotted. The chemical compositions measured at the tip, middle, and root parts are almost the same: B:N:O:Ni =68:28:2:2 (at. %). This apparent deviation from stoichiometric composition is considered to be due to the B signal from the predeposited boron layer on the substrate, which was detected because of the short BN deposition time of 10 min. We suppose that the thin film thickness also caused the detection of the Ni signal from the substrate to be influential. Therefore, we believe that this result does not show the true chemical composition of the fiber itself. It is noteworthy that we did not find a distinct increase of Ni in the chemical composition on the tip in comparison with the rest. From these results we conclude that they have grown with the help of laser light by a mechanism other than vapor - liquid - solid[6] or metal-catalytic mechanism[7] because of (1) little indication of residual metal on the fiber tip and (2) their growth on a pure Si(100) substrate without the help of a metal catalyst.

It should be noted that our BN microfibers form a different category from the BN nanotubes that were first prepared by using arc discharging with catalytic metal(s),[8–10] considering the diameters are hundreds to thousands of times larger than those of BN nanotubes. The growth of a fiber with a constant diameter may be possible when reactive growing sites are exclusively limited and maintained on the tip during the growth. This idea leads us to imagine that the fiber has a kind of (monolithic?) structure with the end of sp^2-bonded BN sheets exposed at the tip. The fast, fibrous growth on the tip is fed by surface diffusion of precursor species from the sidewall where the surface density of the precursor species has a decreasing gradient towards the tip due to the growth reactions taking place at the tip. It is pointed out that with the fiber radius r and the mean surface diffusion length L, the fibrous growth rate may be L/r times the direct impingement rate on the tip, and this factor may be large enough to bring about the fibrous growth.[11] The future applications of these fibrous BN are as yet unknown, but fiber-reinforced materials are one of the possible candidates[12] when mass production is made possible.

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