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Growth process of vertically aligned single-walled carbon nanotubes

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Abstract

Vertically aligned single-walled carbon nanotube films up to 5 μm thick were produced by an alcohol CVD process, in which hydrogen was supplied during the heating-up stage only. A time-progressive investigation of the growth process was performed based on FE-SEM images of SWNT films grown for different CVD times. Measurements of the film thickness by SEM and optical absorbance showed a non-linear growth rate. In situ monitoring of the SWNT film thickness was achieved by measuring the intensity of the laser light passing through the sample, and using the relationship between light absorbance and film thickness.

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1. Introduction

Novel electronic, optical, and mechanical properties [1] of single-walled carbon nanotubes (SWNTs) have provided great potential for a wide variety of applications [2,3]. One of the difficulties in development of practical devices has been the control of SWNT morphology. Until recently, alignment of SWNTs was only achieved parallel to the substrate in the presence of strong electric or magnetic fields [4-6]. However, high-density deposition of Co catalyst using a liquid dip-coat method [7] combined with the alcohol CVD method [8] has shown to produce dense, uniform, and vertically aligned SWNT films over square-centimeter areas [9]. In this Letter, we investigate the growth process of these vertically aligned SWNT films based on time-progressive SEM observations and optical absorption measurement. In situ monitoring of the vertically aligned SWNT film thickness has been made possible by using the nearly linear relation between optical absorbance and the film thickness.

2. Experiments

Vertically aligned SWNTs were grown on quartz substrates (Fig. 1) [9] using the alcohol catalytic CVD process [8]. The catalyst was supported on a quartz substrate, which was dip-coated into a Co-Mo acetate solution (both 0.01 wt% in ethanol) [10]. The catalyst was oxidized by heating the dip-coated substrate in air at 400 ºC, and then reduced in a flowing Ar/H_2 mixture (3% H_2) during heating of the CVD chamber. Catalyst prepared by this method resists agglomeration at the growth temperature (800 ºC), resulting in densely deposited (~10^{17} m^{-2}), mono-dispersed catalyst particles with diameters of 1-2 nm [11]. When the CVD chamber reached 800 ºC, the Ar/H_2 mixture was stopped and ethanol vapor (99.5 % dehydrated ethanol with maximum 0.005 % water) was introduced at 10 Torr to initiate SWNT growth. When we first reported vertically aligned growth [9], we had believed addition of hydrogen as a catalyst activator during CVD was essential, but it has been found to be unnecessary. The background vacuum and low leak turned out to be important as discussed below. Under the low-leak condition, SWNTs grown without the addition of hydrogen were better aligned and in a higher yield than those grown with added hydrogen.

3. Results and discussion

3.1. Growth process of a vertically aligned SWNT film

A series of time-progressive images taken at various growth times are shown in Fig. 2. In the first several seconds of growth, SWNTs form bundles with neighboring tubes. In Fig. 2(a), significant bundling can be seen after only 15 s. At this point, the SWNTs are not yet well aligned but are clearly standing rather than growing along the surface. We attribute this initial vertical growth to a high local tube density, which restricts the growth in all lateral directions. The film thickness at this point is $\approx$200 nm, but much longer bundles can be seen extending above the film. After 1 min of growth [Fig. 2(b)] the SWNT film is now aligned perpendicular to the substrate surface and nearly 1 µm thick. After 10 min of growth [Fig. 2(d)] the aligned film is more than 4 µm thick, but after 30 min [Fig. 2(e)] we find an unexpected slight decrease to 3.9 µm, and after 100 min [Fig. 2(f)] the thickness further decreases to $\approx$3.5 µm. This reduction in thickness is ascribed to the insufficient background vacuum in our CVD chamber, as discussed below.

Resonance Raman scattering spectra taken from some of these SWNT samples (Fig. 3) show high purity of SWNTs, as indicated by the small D-band near 1350 cm^{-1}. The shape of the radial breathing mode (RBM) below 300 cm^{-1} changes only slightly with CVD time; this indicates vertical alignment from the initial stage of growth. The RBM signal observed using a 488 nm excitation laser shows strong peaks at 145, 180, 242, and 257 cm^{-1}. These peaks are characteristic of the RBM signal measured from the top of the sample, and they are attributed to excitation by light polarized perpendicular to the SWNT axis [12]. On the other hand, RBM peaks at 160 and 203 cm^{-1} are due to parallel-polarized excitation of the SWNTs [12]. The small decrease in these peaks with time suggests slightly better alignment at longer CVD times.

Optical absorbance measurements were also performed with laser light incident normal to the substrate on which the aligned SWNT films were grown. As shown in Fig. 4, a decrease in the absorbance after long CVD times agrees with the measured decrease in SWNT film thickness, and a good correlation is observed between the film thickness and the absorbance. Based on this relationship it is possible to determine the thickness of an aligned SWNT film simply by measuring its absorbance. Such a measurement can only estimate the average film thickness over a local area, but its non-destructive nature is advantageous for quality control purposes in a production process.

3.2 Growth-limiting mechanism

Three possible mechanisms limiting the growth are impeded diffusion, catalyst poisoning, and burning of the SWNTs. It has been surmised that these SWNTs are produced by a base-growth mechanism where the catalyst particles remain on the substrate surface during growth [13]. Seemingly, the dense film of SWNTs itself is thought to act as a diffusion barrier, which could cut off some of the supply of carbon-containing ethanol to the catalyst below. However, this effect is estimated to be insignificant for SWNT films with a thickness of only a few micrometers. In addition, for every mole of ethanol that reacts with catalyst on the surface, several moles of reaction products must diffuse away in order for further reactions to continue. This may also cause a reduction in catalyst activity.

Recall that Ar/H_2 was present during heating of the reaction chamber for activation of the catalyst. When the CVD background vacuum is insufficient, oxygen or water can enter the chamber and re-oxidize the catalyst. This reaction, known as catalyst poisoning, decreases the growth rate. We have confirmed that this decrease in the SWNT film thickness can be suppressed by enhancement of the background vacuum in the CVD chamber. Further improvement of the vacuum is desirable to achieve thicker growth of the SWNTs films. This illustrates the importance of thorough catalyst reduction in SWNT growth. The presence of hydrogen helps to counter this oxidation, but it is unnecessary if sufficient background vacuum is attained.

The above-mentioned effects could eventually lead to a zero growth rate for a very thick film, but they do not explain the observed negative growth rate. At 800 ºC, oxygen present in the CVD chamber can burn away the SWNTs by oxidation. This is a negative growth rate, but it is not a significant factor if the catalyst activity is high. A simple qualitative model illustrating these effects is shown in the inset in Fig. 4.

3.3 In situ measurement of film growth

In the nearly linear relationship between light absorbance at 488 nm and the film thickness shown in Fig. 5a, the thickness denotes that on one side of the substrate, whereas the actual thickness through which the light passes is twice this value because SWNT films grow on both sides of the substrate. With this relation, we performed in situ absorbance measurements of the film during 10 min of CVD by passing a 488 nm laser through a quartz substrate placed in the CVD chamber, as shown in Fig. 5b. The relation in Fig. 5a is used to estimate the time-progressive film thickness.

4. Summary

We have shown that vertically aligned SWNT films can be produced without addition of hydrogen during growth. The film thickness is observed to increase non-linearly with CVD reaction time. An eventual decrease in the SWNT film thickness, observed for longer growth times, is attributed to catalyst poisoning and burning of the SWNTs due to excessive oxygen or water in the CVD chamber. Optical absorbance by SWNT films is found to behave similarly to the film thickness as growth proceeds. A nearly linear relationship is observed between the light absorbance and the SWNT film thickness, except in the very early stage of growth. By use of this relationship, measurement of the absorbance of laser light passing through a sample in the CVD chamber has enabled in situ monitoring of the growth of the SWNT film thickness.

The present findings indicate the crucial importance of thorough catalyst reduction for the growth of vertically aligned SWNT films.

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Figure Captions

Fig. 1. A uniform film of vertically aligned SWNTs grown on a quartz substrate. The insert, which corresponds to the area enclosed by the white box, shows the film is approximately 5 μm thick.

Fig. 2. Growth of aligned SWNT films after (a) 15 s, (b) 1 min, (c) 3 min, (d) 10 min, (e) 30 min, and (f) 100 min. Vertical growth of bundles occurs early and causes alignment of the SWNT film. After 10 min the film thickness exceeds 4 μm, but the thickness decreases after longer reaction times. The scale bar applies to all images.

Fig. 3. Resonance Raman spectra excited by 488 nm laser corresponding to (a), (b), (d), and (f) in Fig. 2.

Fig. 4. A plot showing the optical absorbance at 488 and 633 nm (left axis) and film thickness measured by SEM (right axis) as a function of growth time. The absorbance and film thickness follow a similar trend, except in the early stages of growth. The insert shows a qualitative plot of the contributing factors to the growth rate, in which the dashed upper line represents the catalyst activity, and the lower dotted line the burning of the film. The solid line shows the net growth rate, which can eventually become negative if burning is significant.

Fig. 5. In situ optical measurement of vertically aligned SWNT film thickness. (a) The relationship between absorbance at 488 nm and film thickness measured by SEM. (b) Results of in situ measurement of 488 nm light absorbance (left ordinate) and thickness of the film on one side of the substrate (right), vs. CVD time.

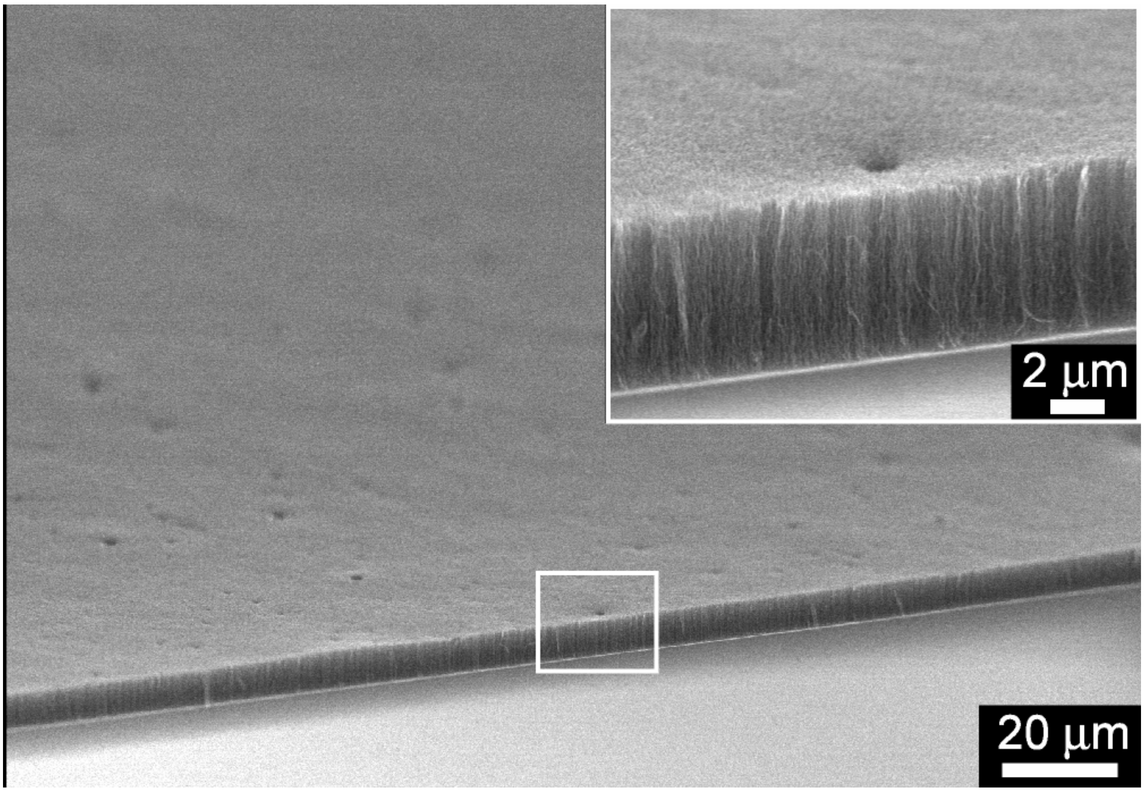


Fig. 1 S. Maruyama et al.

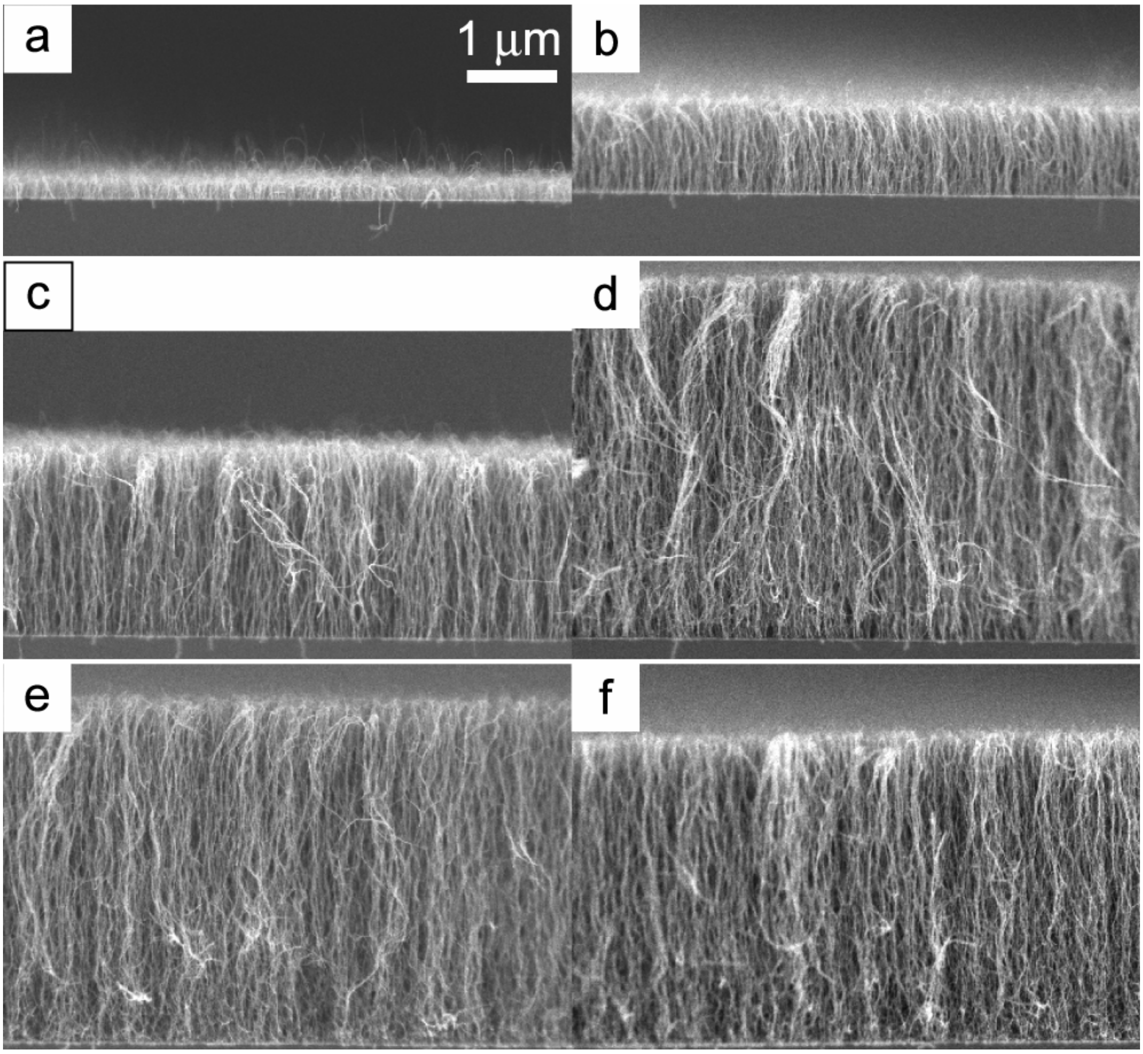


Fig. 2 S. Maruyama et al.

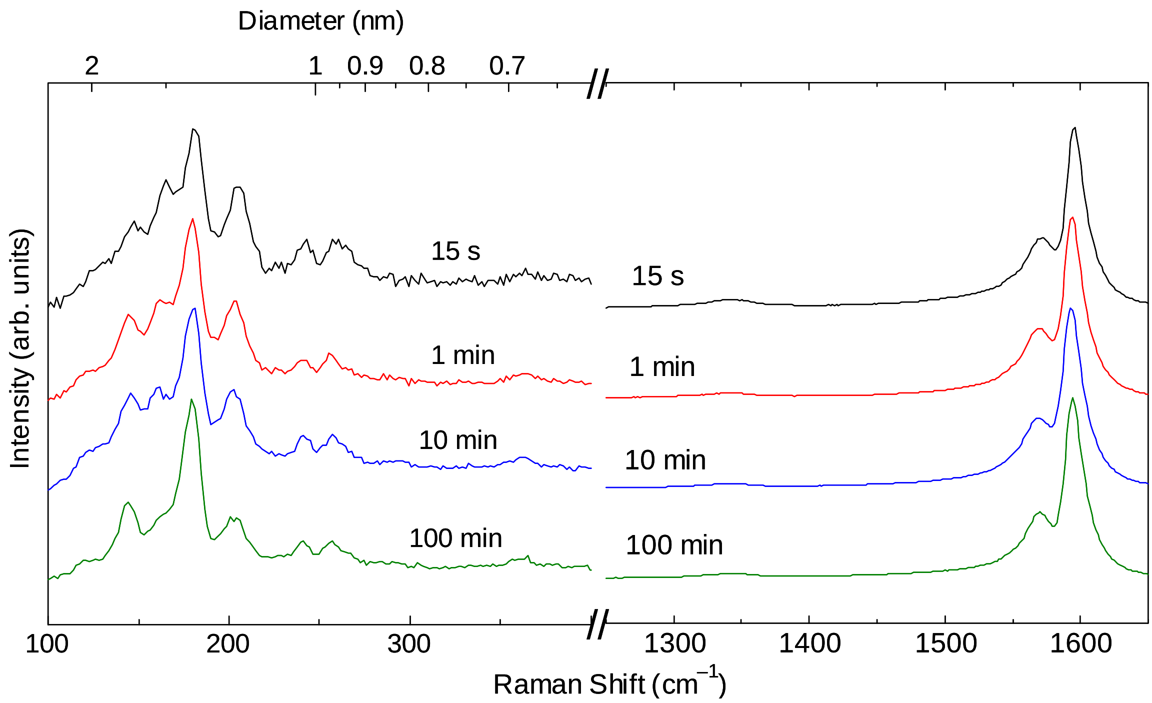
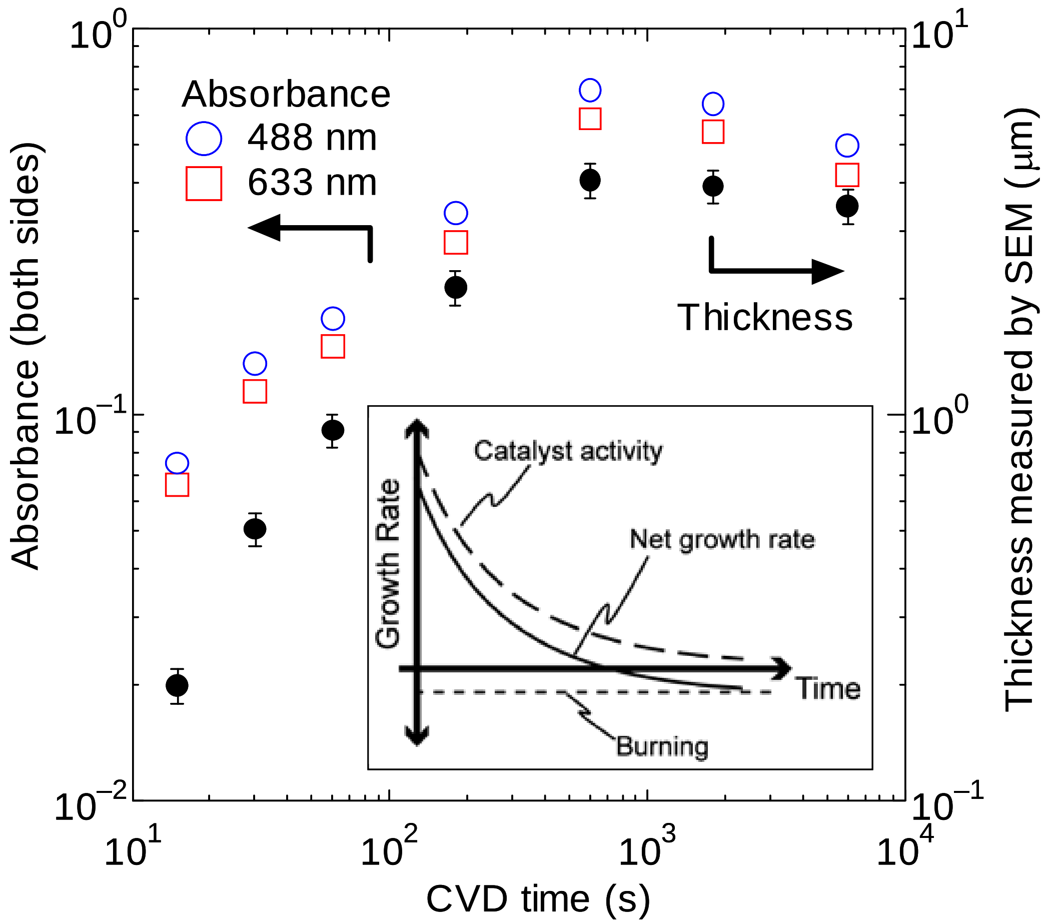


Fig. 3 S. Maruyama et al.



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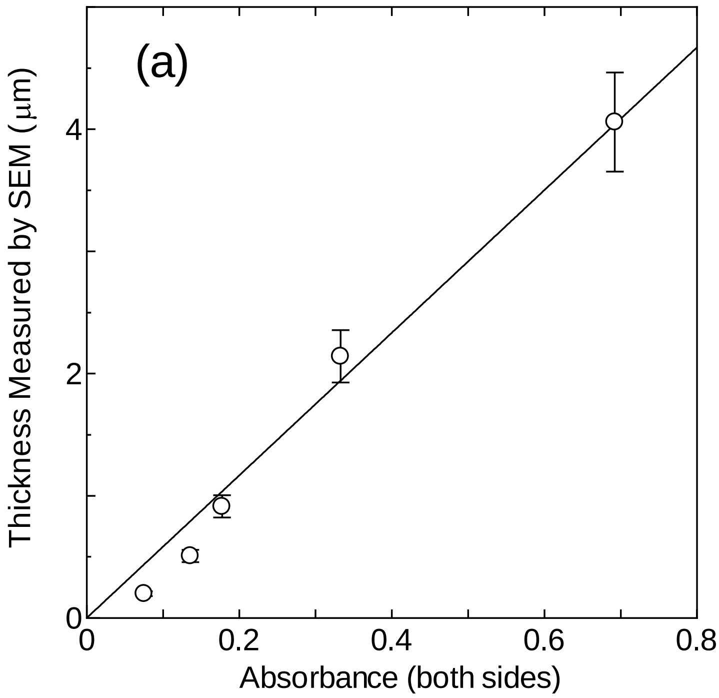

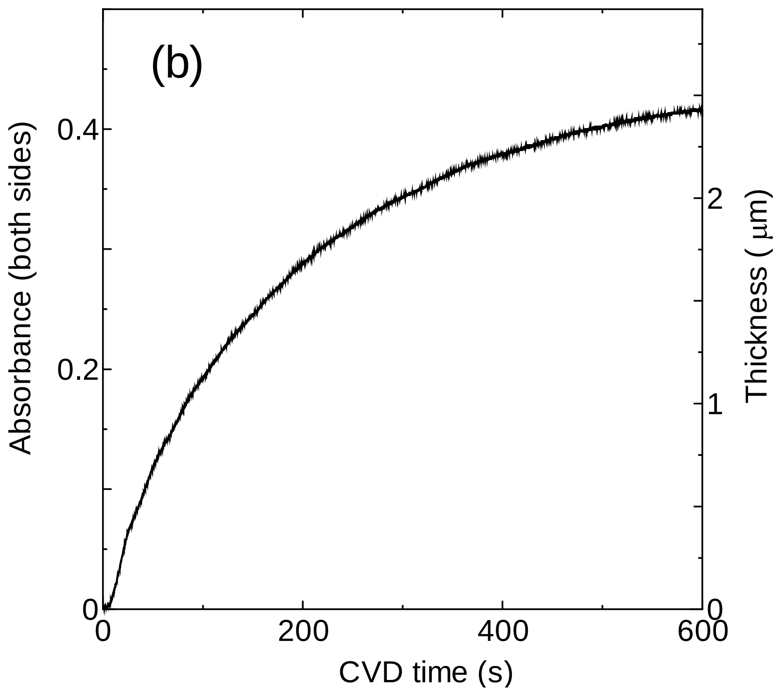

Fig. 5 S. Maruyama et al.