Improvement of the partial electron yield method in the higher-energy soft X-ray XAFS measurement

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Abstract

New micro channel plate (MCP) electron detector for the soft X-ray absorption spectroscopy (XAS) was designed and constructed in order to improve the partial electron yield (PEY) method using a conventional MCP detector. The Si K-edge XAS spectra using a conventional MCP detector was deformed by unexpected fluorescent X-rays, but that using developed MCP detector was hardly affected by fluorescent X-rays. In addition, the PFY method using the detector with suitable bias voltage was more surface sensitive than the total electron yield method. The sampling depth was estimated about 30 nm by Si K-edge XAS measurements of thermal-oxidized Si wafers.

1. Introduction

In the soft X-ray absorption spectroscopy (SX-XAS), the total electron yield (TEY) recording a sample drain current and the partial electron yield (PEY) using an electron detector are adopted as the detection methods in many cases. A typical electron detector for the PEY measurement is composed of two mesh grids for ground and retarding voltages, micro channel plates (MCP), and a collector [1]. Compared with the TEY method, the PEY method using the MCP detector with appropriate bias voltages is more surface-sensitive and less affected by background. Therefore this method provides us high quality spectra, is used in many SX-XAS studies, especially in the lower-energy soft X-ray region ($h\nu$ = 50 – 1000 eV). However it may sometimes cause a serious problem. It is well known that MCPs detect not only electrons but also X-rays. When one uses the MCP detector as an electron detector in XAS measurements without noticing the existence of fluorescent X-rays, one would get a spectrum deformed by unexpected fluorescent X-rays. In the lower-energy soft X-ray region, the effect of fluorescent X-rays might be negligible. However, it becomes non negligible in the higher-energy soft X-ray region ($h\nu$ = 1000 – 4000 eV), since the core hole decay with the fluorescent process increases to some extent, though the Auger decay process is still dominant. In order to overcome this problem, it is necessary to develop a new electron detector instead of the conventional MCP detector.

We have designed and constructed a new MCP electron detector based on the MCPs for improvement the above problem. We propose a SX-XAS detection system using the new detector including the higher-energy soft X-ray region.

2. Experimental

Fabrication of a new SX-XAS detection system and all the XAS measurements were performed at the SR center, Ritsumeikan University, using the soft X-ray double crystal monochromator beamline (BL-10) [2]. Developed MCP electron detector was used in high-vacuum measurement chamber kept less than 5×10^{-8} Torr. Same kinds of MCPs (Long-life Microchannel Plates, Photonis USA, USA), which is the detecting area of 25 mm diameter and the aspects ratio of 60:1, were used as main components of the detector.
As the samples for evaluating the detectors, a Si wafer etched in 1% aqueous solution of HF (HF-Si) and several thermal-oxidized Si wafers (SiO_2/Si) with different SiO_2 film thickness were prepared. The thickness of the SiO_2 layer of each sample was controlled by the heating time and temperature and monitored by the ellipsometry (λ = 633 nm), in which the refractive index was fixed to 1.457 [3].

Si K-edge XAS measurements were performed for these samples. A pair of InSb(111)

crystals were used as monochromatizing crystals. As the energy reference, the white line of quartz (1846.8 eV) was used [4]. Partial fluorescence yield (PFY) spectra were measured using silicon drift detector (SDD: XFlash detector, series 1201, Rontec, Germany) whose detecting area is 5 mm^2. TEY spectra were measured using sample drain current in this study.

3. Results & Discussion

3.1 Si K-edge XANES spectra with the TEY method

The Si K-edge XAS measurement by the TEY method had been performed in order to be confirmed the sampling depth of a SiO_2/Si sample by the TEY method before that by the PFY method using detectors was performed. Figure 1 (a) shows observed Si K-edge XANES spectra of HF-Si and SiO_2/Si with several different SiO_2 thicknesses, obtained by the TEY method using a sample drain current. As the SiO_2 thickness increases, a near edge peak at 1840 eV is gradually suppressed, while a feature at 1847 eV gains the intensity. The HF-Si sample gives the spectrum of a Si, and the fully oxidized Si sample (127.8 nm SiO_2/Si) gives the spectra of SiO_2. The spectra from 14.6 to 76 nm SiO_2/Si can be regarded as a superposition of the above two typical spectra. Spectral analysis of these two contributions to each spectrum gives an intensity ratio of Si and SiO_2, which are plotted in

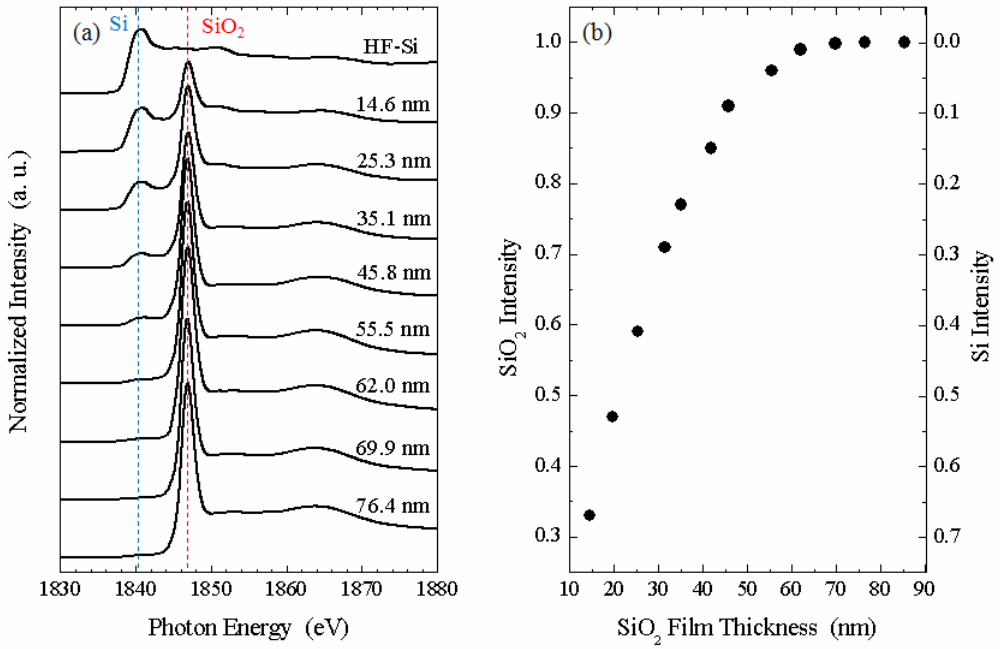

Fig. 1. (a) Observed Si K-edge XAS spectra by the TEY measurement of HF-Si and SiO_2/Si as a function of SiO_2 film thickness and (b) intensity ratio distribution between Si and SiO_2 in each observed XAS spectra.

Figure 1 (b). From these plots, the sampling depth at Si K-edge by the TEY measurement using the sample drain current was estimated to be about 70 nm, which is in good agreement with that of M. Kasrai et al. [4].

3.2 Si K-XANES with a conventional MCP detector

Figure 2 shows a schematic drawing of an arrangement for the PEY method using conventional MCP detector. The conventional MCP detector was placed under the sample in order to prevent from elastic X-rays [1]. The distance between the sample and MCPs was about 40 mm in this experimental setup. Figure 3 (a) shows observed Si K-edge XAS spectra of 100 nm SiO_2/Si taken with the conventional MCP detector as a function of bias voltages. Compared with the TEY spectrum, the XAS spectrum at the bias voltage = 0 V shows a weak but distinct feature of bulk Si. By increasing the bias voltage, the feature from bulk Si is more enhanced. It is generally believed that the PEY method with a bias voltage gives surface sensitive spectra. However, above results just contradict with the general tendency.

In order to explain this phenomenon, we show how the bias voltage changes the spectrum in Figure 3 (b). As the bias voltage increases, the peak associated with SiO_2 decreases drastically, but the peak with bulk Si does not change at all (see inset of Figure 3 (b)), even when a high bias voltage (-2000 V) was applied enough to repel all emitted electrons from the sample. It tuned out that the origin of the peak at 1840 eV is fluorescent X-rays from bulk Si. This result indicates that observed XAS spectra using the conventional MCP detector are composed of the spectrum by the PEY measurement and that by the total

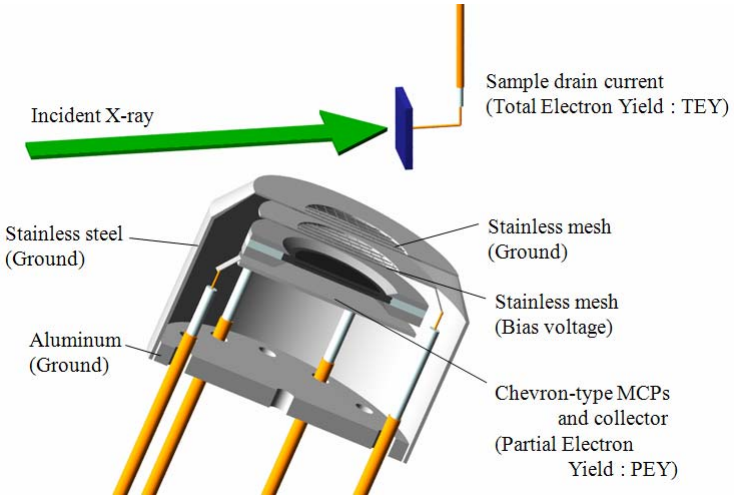

Fig. 2. The schematic drawing of the typical MCPs detector and the arrangement of the sample, incident X-rays, and detectors.

fluorescence yield (TFY) measurement. By increasing the bias voltage, number of detected electrons decreases, but that of fluorescent X-rays does not change. As the result, the TFY signal is relatively enhanced and apparently the MCP detection gives a bulk sensitive detection at high bias voltage. In other words, a PEY spectrum is deformed by unexpected TFY spectrum, especially in the higher-energy soft X-ray region.

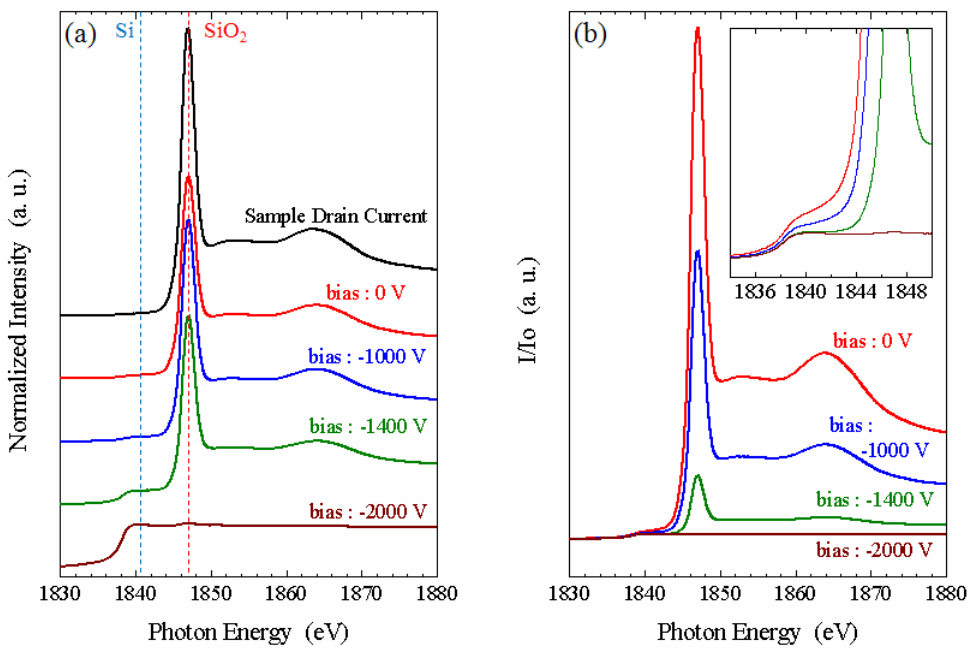

Fig. 3. (a) Observed Si K-edge XAS spectra of 100 nm SiO_2/Si using the conventional MCP detector at several bias voltages, and (b) intensity ratio distribution of SiO_2 and Si as a function of bias voltages.

3.3 Development of a new detector system

From the result of the previous section, we found it necessary to make the influence of fluorescent X-rays as small as possible for the PEY method using an electron detector. A newly-developed MCP electron detector was designed and constructed to overcome this problem. The schematic drawing, picture and schematic diagram of the new MCP electron detector are shown in Figure 4. There are two major modifications from the conventional MCP detector. The first is that the trajectory of emitted electrons from a sample is changed, and the electrons are detected by MCPs. For this purpose, three cylindrical stainless grids (transmission rate: 77.8 %) were used with applied bias voltage of -3000 V between the inner and the center grid to deflect electron trajectories. The role of the outer grid is to prevent from a leak voltage. The second is to place a dish-like stainless steel plate between the sample and MCPs, so as to avoid direct irradiation of MCPs by fluorescent X-rays.

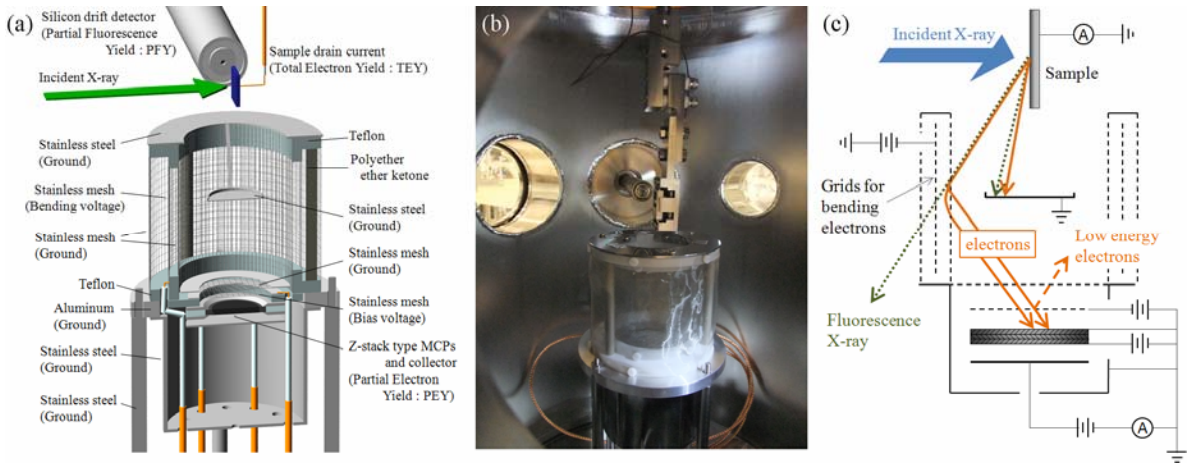

Fig. 4. (a) The schematic drawing, (b) the picture in the measurement chamber and (c) schematic diagram of newly-developed MCPs electron detector and the arrangement of sample, incident X-ray, and detectors.

Accepted elevation angle of this electron detector was about 30 ± 5 degrees.

Figure 5 (a) shows observed Si K-edge XAS spectra of the 25.3 nm SiO_2/Si as a function of the bias voltage, together with the TEY spectrum. Compared with the TEY spectrum, the PEY spectrum without the bias voltage is slightly surface sensitive. This is the reason why detectable elevation angles of emitted electrons are limited by the MCP detector construction.

Figure 5 (b) shows how the intensity ratio of SiO_2 and Si of the observed XAS spectra

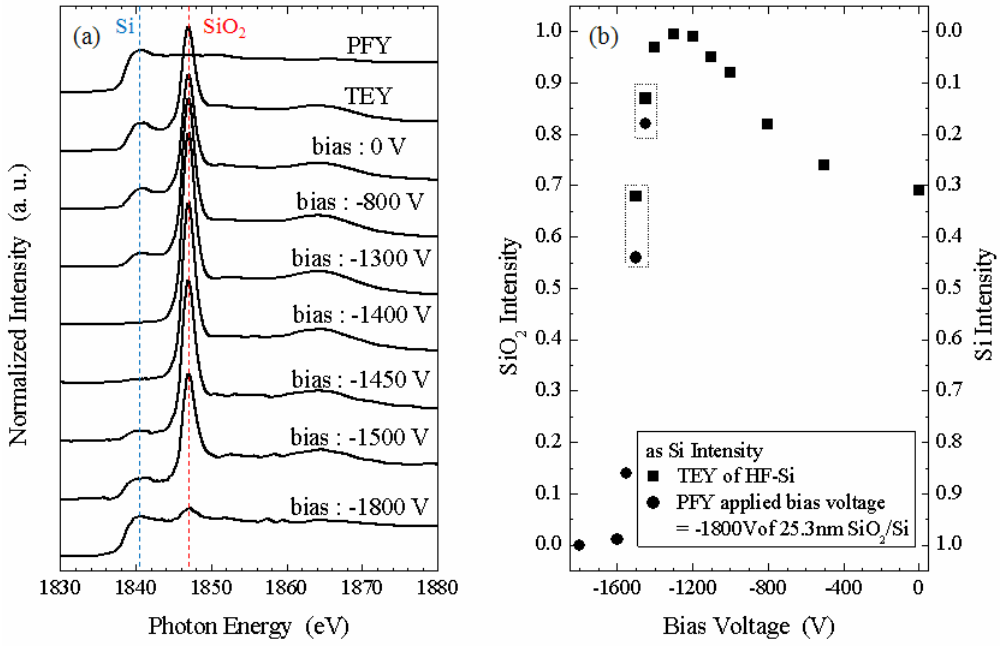

Fig. 5. (a) Observed Si K-edge XAS spectra of 25.3 nm SiO_2/Si at several bias voltages, and (b) intensity ratio distribution of SiO_2 and Si as a function of bias voltages.

changes as a function of bias voltage. Here two kinds of spectra were used to stand for bulk Si; the TEY spectrum of HF-Si (filled circles) and that of 25.3 nm SiO_2/Si at the bias voltage of -1800 V (filled squares). This reason is explained below. As the bias voltage were increased from 0 to -1300 V, SiO_2 intensity increased and Si intensity decreased. This is an expected result for the PEY measurements unlike that of the conventional MCP detector. As the bias voltage was increased further from -1300 to -1800 V, SiO_2 intensity decreased and bulk Si intensity increased. Si KLL Auger electrons could not reach the detector at the bias voltage of -1800 V. This means that there is still the influence of fluorescent X-rays in this system. Possibly, fluorescent X-rays and electrons emitted from the sample collide with stainless grids and generate lower energy fluorescent X-rays, such as Fe, Ni and Cr Lα emission, which are detected by the MCP detector. Thus, the XAS spectrum at the bias voltage of -1800 V also stands for bulk Si. However the influence is very small and can be neglected in the case of the bias voltage less than -1300 V, because it needed to increase the MCP voltage from +2400 V to +3200 V rapidly in order to detect signals when bias voltages were applied more than -1300 V. Above results indicate that the suitable bias voltage at Si K-edge is -1300 V.

Then, we estimated the sampling depth at the Si K-edge. Figure 6 (a) shows observed Si K-edge XAS spectra of SiO_2/Si as a function of SiO_2 film thickness using the PEY method with the bias voltage = -1300 V. As the SiO_2 film thickness increases, the intensity

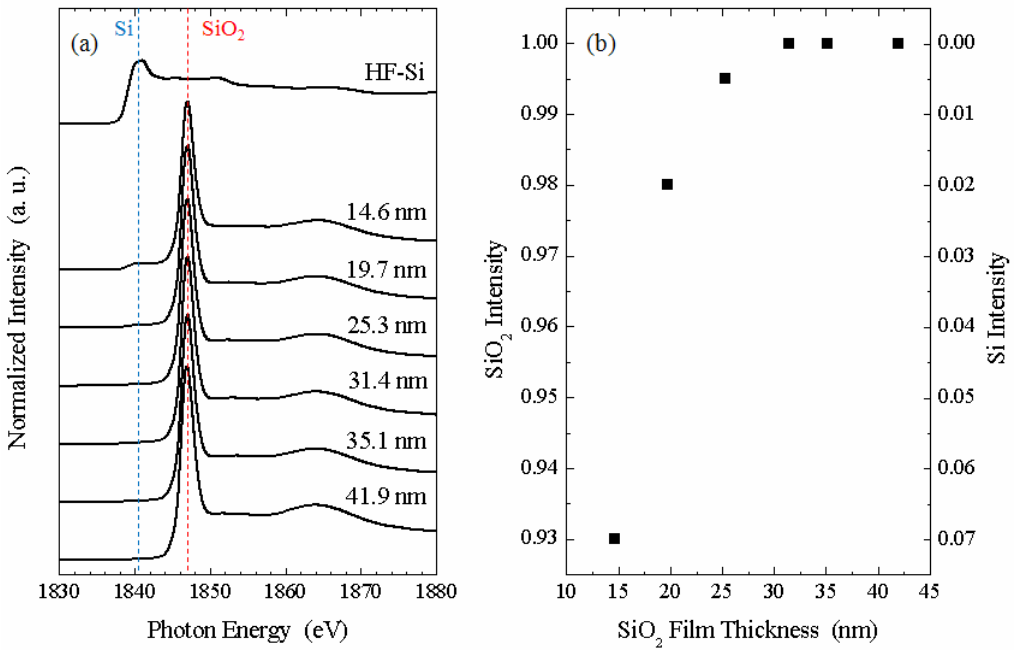

Fig. 6. (a) Observed Si K-edge XAS spectra of SiO_2/Si as a function of SiO_2 film thickness by PEY methods with the bias voltage = -1300 V, and (b) intensity ratio distribution between SiO_2 and Si in each PEY spectra.

of the SiO_2 peak increases rapidly and is saturated, as shown in Figure 6 (b). From this intensity ratio profile, the sampling depth at Si K-edge of the PEY was estimated to be about 30 nm in SiO_2/Si system. This is less than half of the sampling depth of the TEY.

Using this developed MCP electron detector enables to detect more surface sensitive than the TEY method, and obtain more detailed information about samples. Figure 7 shows XAS spectra taken simultaneously with the PEY method using developed MCPs electron detector with the bias voltage = -1300 V, the TEY method using sample drain current, and the PFY method using SDD, which give us the information about surface, interface and bulk, respectively. (Note that the self-absorption effect was not corrected in the PFY spectrum.) This SX-XAS detection system is not only useful to obtain more information about a sample but important for an XAFS measurement at a synchrotron radiation facility with limited available measurement time.

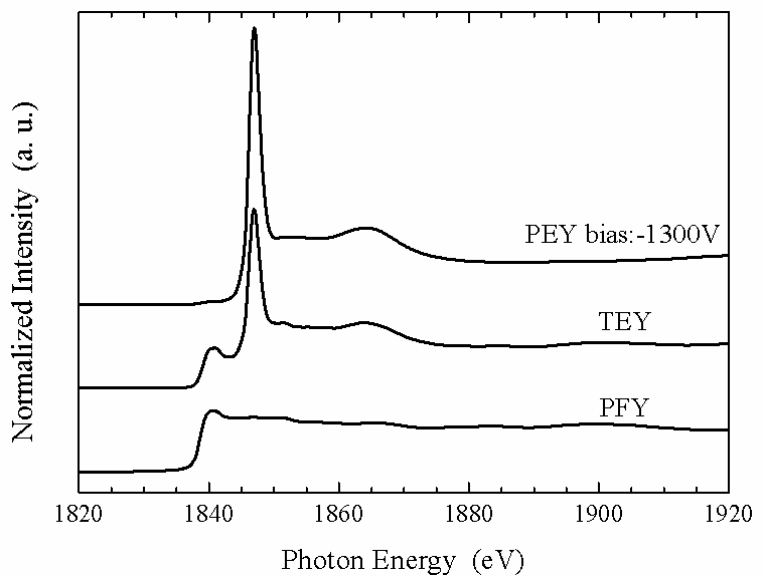

Fig. 7. Observed Si K-edge XAS spectra of 25.3 nm SiO_2/Si taken simultaneously with the PEY method using developed MCP electron detector with the bias voltage = -1300 V, the TEY method using sample drain current, and the PFY method using SDD.

4. Summary

We have designed and constructed a new MCP electron detector in order to overcome the serious problem, in which of a PEY spectrum using the conventional MCP detector was deformed by unexpected TFY spectrum in the higher-energy soft X-ray region. PEY spectra measured by the developed detector with bias voltage at -1300 V were hardly affected by fluorescent X-rays, and more surface sensitive compared with that of the TEY. We expect that this new SX-XAS detection system becomes one of standard methods.

Acknowledgements

This work was supported by Research and Development Initiative for Scientific Innovation of New Generation Batteries (RISING) project from New Energy and Industrial Technology Development Organization (NEDO) in Japan and by Nanotechnology Network (Nanonet) Project from Ministry of Education, Culture, Sports, Science and Technology (MEXT) in Japan. The authors are grateful to them.

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