Chemical Structure Changes in TOPO Capped CdSe Nanocrystals Thin Films by Comparable ToF-SIMS and XPS Study

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Comparable characterization of trioctylphosphine oxide (TOPO) capped CdSe nacocrystals by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are demonstrated. Quantitative analysis of surface elemental composition and chemical state for CdSe nanocrystals surface was performed with XPS. Qualitative information about the surface complex formed on the CdSe was extracted from the ToF-SIMS spectra. Based on the results obtained, the mechanism of the photon-induced changes in TOPO capped CdSe surface was proposed as follows: In the initial state, organic ligand TOPO bound to Cd site on the CdSe surface, which was deduced from the detection of (TOPO+Cd) cluster ions. In the photo-brightening state, where photoluminescence (PL) intensity increased after some amount of illumination, a part of TOPO migrated from Cd site to Se site forming TOPO-Se complex. In the photo-darkening state, where the PL intensity gradually decreased after the photo-brightening, oxidation of surface Se and decomposition of TOPO-Se complex occurred, which was followed by the desorption of TOP and SeO_2 from the surface. It is proved that XPS and ToF-SIMS can be used for surface chemical structure analysis as complementary techniques.

1. Introduction

Chemically synthesized semiconductor nanocrystals (quantum dots) whose radii are smaller than the bulk exciton Bohr radius exhibit unique optical properties [1]. Quantum confinement of both the electron and hole in three dimensions leads to an increase in the effective band gap of the material with decreasing crystal size. Both the optical absorption and emission energies of quantum dots shift to the blue side (higher energy) as the size of the dots gets smaller.

The optical properties of CdSe nanocrystals are being extensively investigated [1-3]. It has been reported that the photoluminescence (PL) intensity of a thin film of CdSe is increased by some duration of UV light irradiation, and that further irradiation of UV light causes gradual decrease in PL intensity [2]. The state where the PL intensity is maximized is called a photo-brightening (PB) state, and the state where the PL intensity is decreased with further irradiation is called a photo-darkening (PD) state. These phenomena enable the invention of the luminescence-based optical memory media.

PL efficiency is deeply correlated with surface state of nanocrystals such as the degree of passivating surface nonradiative recombination sites or adsorption state of organic ligand. Recently the changes in surface states of CdSe nanocrystals before and after the irradiation of blue light have been investigated by surface analytical tools of X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) [3]. In this paper, we demonstrate that the complementary information can be obtained on the changes in surface chemical structure of trioctylphosphine oxide (TOPO) capped CdSe nanocrystals by XPS and ToF-SIMS and that the combination of XPS and ToF-SIMS is a very powerful method for microscopic chemical analysis for surfaces.

2. Experimental

2.1. Materials

Synthesis of CdSe nanocrystals

TOPO-capped CdSe nanocrystals used were prepared by the colloidal chemical method [1]. A mixture of dimethylcadmium and selenium, dissolved in tributhylphosphine (TBP), was rapidly injected into TOPO which was heated up to 300-350 degree C. The diameter of CdSe nanocrystals thus prepared was about 3.5 nm, which was confirmed by transmission electron microscopy (TEM). The synthesized nanocrystals were dissolved in $CHCl_3$ and the solution was spin-coated onto a Si wafer and dried in vacuum at room temperature.

Optical properties

A fluorescence microscope equipped with an optical multichannel analyzer was used to measure the intensity of PL excited by He-Cd laser (442 nm), whose power density was about 1 W/cm^2. The PL inensity of CdSe nanocrystals is plotted as a function of He-Cd laser irradiation time in Fig.1(a). The PL intensity rapidly increased up to 1 min and decreased gradually for further irradiation. In this paper, the PB state and PD state were prepared by the irradiation of He-Cd laser light for 1 min and 30 min, respectively. The irradiated area was the order of cm. In Fig.1 (a), the peak position of PL spectra is also plotted, and a gradual blue shift of the peak with increasing irradiation time was clearly observed. Optical properties of the samples in the initial, PB and PD state are summarized in Fig.1(b).

2.2. Surface characterization

To investigate the change in surface states among initial, PB and PD states, Auger electron spectroscopy (AES), XPS and ToF-SIMS measurements were performed.

AES measurements

A VG Microlab 310-F system was used for AES measurements in order to analyze qualitatively the composition in the surface region of the CdSe nanocrystals films. Auger electrons were excited by Schottky-type field emission gun (FEG), operating at energy of 10 keV and current of 6.5 nA, and detected with a concentric hemispherical analyzer (CHA). The detection angle was 30 degree from the surface normal. The energy resolution of $\Delta E/E$ was 0.5% for wide-scan spectra, 0.2% for narrow-scan spectra of Cd MNN and 0.1% for narrow-scan spectra of Se LMM. In this system, AES spectra with high energy resolution can be obtained and directly compared with XPS spectra. In XPS spectra, both the peaks of photoelectrons and Auger electrons are observed, while electron-excited AES spectra provide the information on only Auger electrons. Thus, comparison of XPS and AES spectra allows us to extract only photoemission peaks from XPS data.

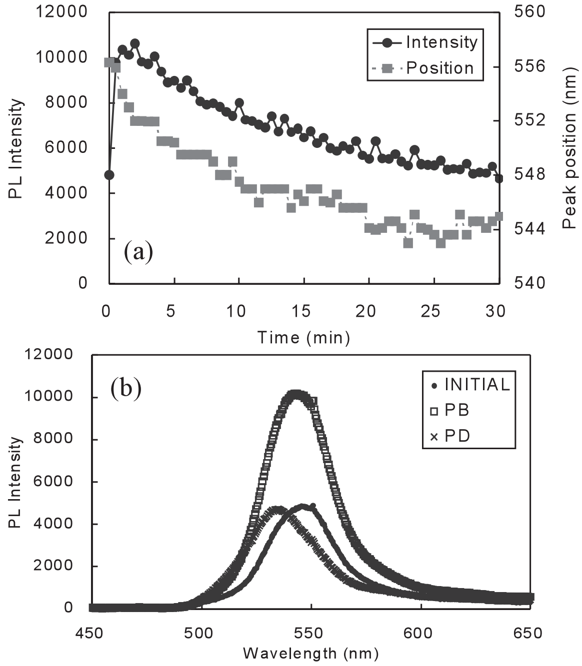

Fig. 1. (a) Variation in PL intensity and peak position as a function of laser irradiation time.
(b) PL spectra of CdSe nanocrystals thin film, in initial, PB and PD states.

XPS measurements

A PHI Quantum 2000 system was used to perform XPS analysis. Photoelectrons and Auger electrons were excited by monochromated Al-Kα and detected with CHA. The X-ray tube was operated at 30 W. The pass energy of CHA was 187.35 eV for wide-scan spectra and 29.35 eV for narrow-scan spectra. The analyzing area on the specimen surface was 500 μm × 500 μm, which was located in the center of the irradiated area. The take-off angle was 45 degree. The binding energies of the spectra are calibrated by setting the C 1s peak maximum at 284.6 eV.

ToF-SIMS measurements

An ION-TOF TOF-SIMS IV system was used for ToF-SIMS measurements. Pulsed Ga ion gun operating at energy of 25 keV, current of 0.5 pA and pulse frequency of 5 kHz was rastered in 300 µm × 300 µm on the specimen surface. Positive or negative secondary ions were detected with reflectron-type mass spectrometer. The acquisition time to obtain a spectrum was typically 240 sec. Under these conditions, total primary ion dose was 8.3×10^{11} ions/cm^2, which is well below the static limit.

3. Results and discussion

3.1. Qualification of surface elements by AES and XPS

XPS and AES wide-scan spectra of the CdSe nanocrystals thin film in the initial state are shown in Fig.2-1. On both spectra, Auger transition lines of C KLL, O KLL, P KLL, Se LMM and Cd MNN are clearly observed and other lines of unexpected elements are not detected. In the XPS wide-scan spectra, there are many peaks arising from Se LMM Auger transitions in the kinetic energy range of 1000-1400 eV and peak interference between Se $L_2M_{45}M_{45}$ and P 2p occurs. Thus, P 2s spectra will be used to analyze the chemical state of P in the following section.

In order to demonstrate the high-energy resolution of the AES facility used in this work, narrow-scan spectra of Cd MNN and Se LMM are shown in Figs.2-2 and 2-3 together with XPS spectra. Here the pass energy was set at 29.35 eV for XPS and the energy resolution was 0.1-0.2% for AES, which reduces the pass energy of CHA to around 38 eV for Cd $M_4N_{45}N_{45}$ and 65 eV for Se $L_3M_{45}M_{45}$, respectively. The electron-excited AES spectra with high-energy resolution have similar line shapes as X-ray-excited spectra. Thus we can use AES as a tool for chemical state analysis as well as conventional XPS. However, since the electron excitation will cause the severe damage to organic molecules, we will use XPS for detailed analysis in the following section.

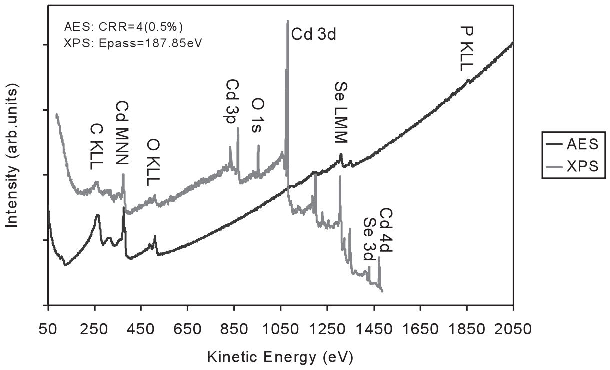

Fig. 2-1 AES and XPS wide-scan spectra from CdSe nanocrystals thin film, in initial state.

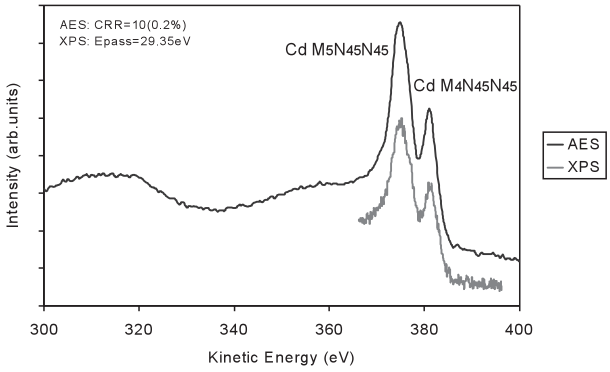

Fig. 2-2 AES and XPS narrow-scan spectra of Cd MNN from CdSe nanocrystals thin film, in initial state.

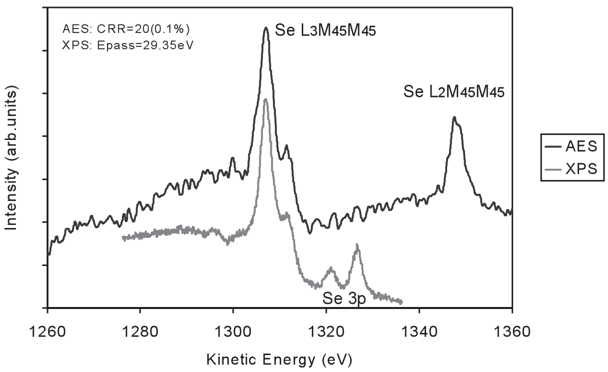

Fig. 2-3 AES and XPS narrow-scan spectra of Se LMM from CdSe nanocrystals thin film, in initial state.

3.2 Quantification of surface atomic composition and chemical state analysis by XPS

XPS narrow-scan spectra of C 1s, O 1s, P 2s, Se 3d and Cd 3d are shown in Fig.3. Auger lines of Cd MNN are also shown in order to examine the change in Cd Auger parameter. Surface atomic composition was evaluated by relative sensitivity factor method via the instrument quantification software, i.e. using the sensitivity factors and a transmission function corresponding to the measuring conditions, which are given by manufacturer. In Table 1, elemental composition of CdSe nanocrystals surface in the initial PB and PD states are tabulated. The C, O and P atoms are components of organic ligand TOPO. With increasing irradiation time, C and P decreased, whereas O increased. There was no sign of the change in chemical states of C, O and P, as shown in Figs.3-1, 3-2 and 3-3. Decrease of C and P, and increase of O are thought to be due to the fact that TOPO ligands are adsorbed on the CdSe surface with the O end, and the laser irradiation dissociates the P-O bond which leads to the desorption of TOP leaving the O atoms on the surface.

Along with desorption of TOP, Se slightly decreased and Cd slightly increased. These changes lead to decrease of the atomic ratio of Se/Cd from 0.55 to 0.50. Whereas there was no significant change in Cd 3d and Cd MNN spectra, the line shapes in Se 3d drastically changed. With increasing irradiation time, the peak around 54 eV originating from Cd-Se decreased and Se oxide peak appeared around 59 eV. Proportion of Se oxide peak in Se 3d was estimated to be 4% in the initial state, 14% in the PB state and 42% in the PD state, respectively. In the PD state, almost half of Se was oxidized.

Table 1. Surface atomic composition (at%) of CdSe nanocrystals thin films.

Sample	C	O	P	Se	Cd
Initial	61.4	16.2	3.7	6.7	12.1
PB	58.4	19.6	2.8	6.5	12.7
PD	53.8	25.0	2.0	6.4	12.8

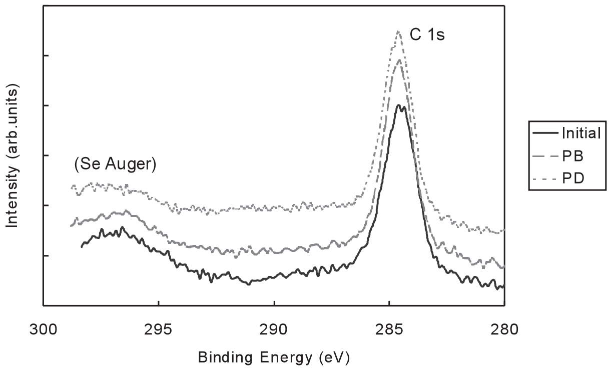

Fig. 3-1 XPS narrow-scan spectra of C 1s from CdSe nanocrystals thin films, in initial, PB and PD states.

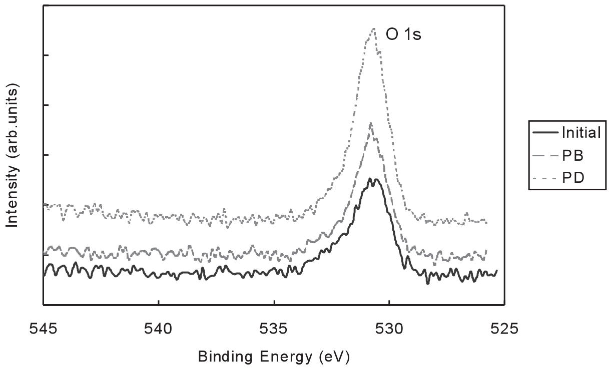

Fig. 3-2 XPS narrow-scan spectra of O 1s from CdSe nanocrystals thin films, in initial, PB and PD states.

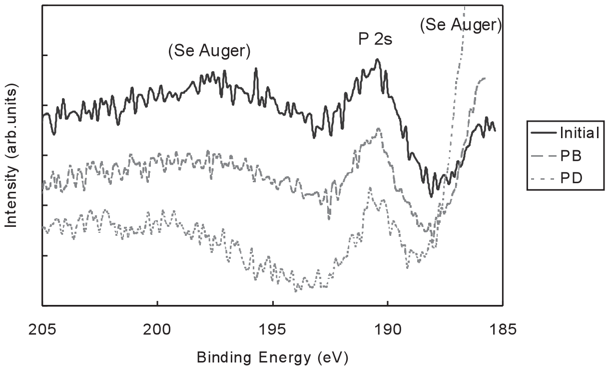

Fig. 3-3 XPS narrow-scan spectra of P 2s from CdSe nanocrystals thin films, in initial, PB and PD states.

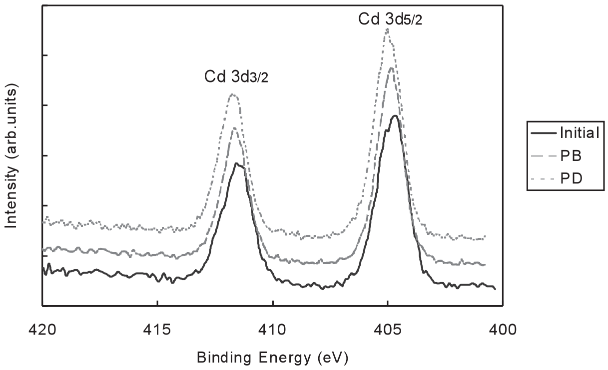

Fig. 3-4 XPS narrow-scan spectra of Cd 3d from CdSe nanocrystals thin films, in initial, PB and PD states.

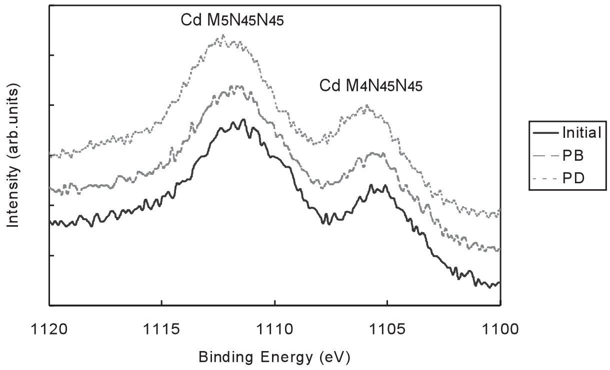

Fig. 3-5 XPS narrow-scan spectra of Cd MNN from CdSe nanocrystals thin films, in initial, PB and PD states.

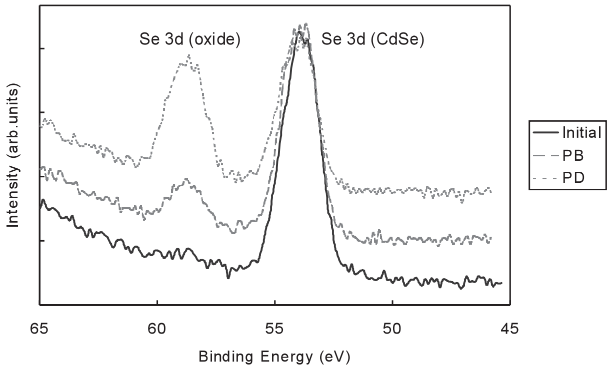

Fig. 3-6 XPS narrow-scan spectra of Se 3d from CdSe nanocrystals thin films, in initial, PB and PD states.

Based on the XPS results obtained, it can be concluded that decomposition of TOPO, desorption of TOP and oxidation of surface Se occurred after the laser irradiation. Here one may address the question: Why did PL intensity increase in PB state? In order to perform the further investigation about the chemical structure of the CdSe nanocrystals surface, we performed ToF-SIMS analysis.

3.3. Chemical structure analysis by ToF-SIMS

Positive ion ToF-SIMS spectra are shown in Fig.4. Intensities of characteristic peaks in the spectra of initial, PB and PD states are summarized in Table 2. The intensities are normalized to those for the initial state. C_xH_y and Cd peaks were dominant peaks in low-mass region (Fig.4-1). Whereas the intensities of Cd peaks were decreased, those of CdOH were increasing with laser irradiation (Fig.4-2). These behaviors are believed to indicate the progress in surface oxidation of Cd [4], which is not clear in the XPS spectra (Fig.3-4). Comparative information on the oxidation index for Cd and Se will be discussed in the following section.

For organic ligand TOPO, its molecular ions (M-H and M+H) were observed at *m/z* 385 and 387, and the peaks were drastically increased in intensity in the PB state (Fig.4-3). Characteristic enhancement of the TOPO molecular ions indicates that TOPO possesses slightly positive charge and the ionization probability of TOPO increases in the PB state. In addition, its dimer ion was observed only in the PB state (Fig. 4-3). Appearance of the dimer ion can be explained to be due to the appearance of high TOPO coverage region on the CdSe nanocrystal surface.

Most interesting results are shown in Fig.4-4. Peaks arising from a TOPO+Cd cluster are observed in Fig.4-4 irrespective of the laser irradiation time, while those from a TOPO+Se cluster are not found in the initial state. These results indicate that TOPO ligands are bound to the Cd sites in the initial state. This adsorption model is reasonable because TOPO is an electron-donating molecule and is thus expected to interact with Cd site. In the PB state, a cluster ion composed of TOPO and Se appeared. Appearance of the TOPO+Se ion indicates the formation of new chemical bonding between TOPO and Se. In summary, above results indicate that the laser irradiation induces migration of some TOPO molecules from Cd sites to Se sites.

Table 2. Characteristic peak intensities on positive ion ToF-SIMS spectra from CdSe nanocrystals thin films, normalized to the initial state.

Positive Ion	Mass	Initial	PB	PD
C_xH_y(x=1-5)		1.000	1.006	1.038
PO	46.97	1.000	0.996	1.077
C_8H_{17}POH	161.11	1.000	1.480	1.254
TBP+OH	219.19	1.000	1.251	1.100
$(C_8H_{17})_2$PO	273.24	1.000	1.172	1.099
TOPO-H	385.36	1.000	1.906	1.397
TOPO+H	387.38	1.000	**5.578**	2.193
$(TOPO)_2$+H	773.75	1.000	**64.750**	6.000
^{80}Se	79.92	1.000	1.218	1.288
^{114}Cd	113.90	1.000	0.901	0.768
^{114}CdOH	130.90	1.000	1.496	**2.357**
TBPO+^{114}Cd	332.08	1.000	1.304	0.854
TOPO+^{114}Cd	500.27	1.000	1.297	0.844
TOPO+^{80}Se+H	467.31	1.000	**23.778**	5.519

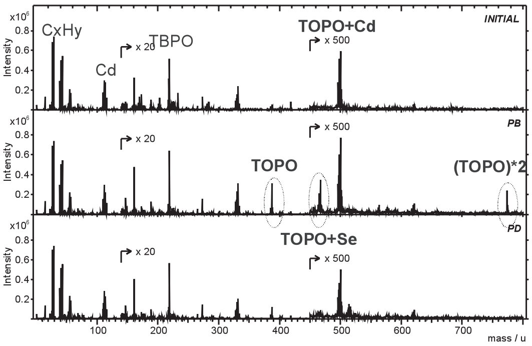

Fig. 4-1 Positive ion ToF-SIMS spectra from CdSe nanocrystals thin films, in initial, PB and PD states.
Overview in the mass range of *m/z* 0-800.

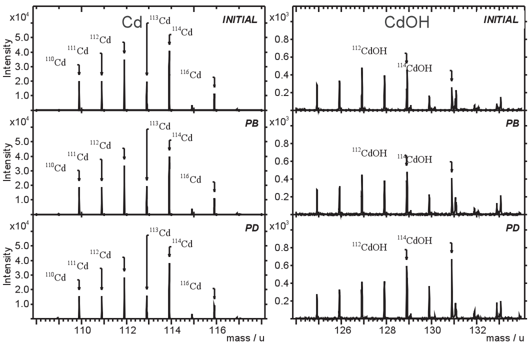

Fig. 4-2 Positive ion ToF-SIMS spectra from CdSe nanocrystals thin films, in initial, PB and PD states.
Zoomed view of Cd^+ and $CdOH_x^+$ regions.

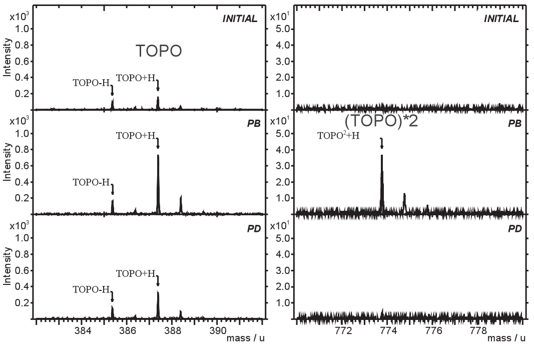

Fig. 4-3 Positive ion ToF-SIMS spectra from CdSe nanocrystals thin films, in initial, PB and PD states.
Zoomed view of TOPO molecular and TOPO dimer ion regions.

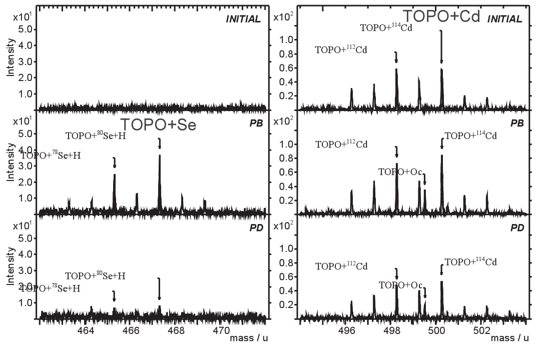

Fig. 4-4 Positive ion ToF-SIMS spectra from CdSe nanocrystals thin films, in initial, PB and PD states.
Zoomed view of TOPO+Se and TOPO+Cd cluster ion regions.

Negative ion ToF-SIMS spectra are shown in Fig.5. Intensities of characteristic peaks in the spectra are summarized in Table 3. The intensities are normalized to those for the initial state. OH_x and PO_x peaks were dominant peaks in low-mass region (Fig.5-1). Whereas the intensities of OH_x peaks were increasing, those of PO_x were decreasing with laser irradiation (Fig.5-2). Increase of oxygen and decrease of PO_x are also deduced from the XPS results.

Negative ion ToF-SIMS is useful especially for the analysis of the chemical state of Se, because Se, one of the electron-donating elements, tends to appear in the negative ion spectra. Negative ion spectra of Se and SeO_x are shown in Figs.5-3, 4. With increasing irradiation time, Se peaks were decreasing and SeO_x peaks were increasing. These behaviors are believed to indicate the progress in oxidation of surface Se, which is consistent with the XPS results (Fig.3-6).

Table 3. Characteristic peak intensities on negative ion ToF-SIMS spectra from CdSe nanocrystals thin films, normalized to the initial state.

Negative Ion	Mass	Initial	PB	PD
OH_x(x=0-1)		1.000	1.128	1.285
PO_x(x=0-3)		1.000	0.939	0.795
$C_8H_{17}P_2O_5$	255.05	1.000	0.889	0.768
$(C_8H_{17})_2PO_2$	289.22	1.000	0.860	0.577
^{80}Se	79.91	1.000	0.619	0.417
^{80}SeO	95.91	1.000	1.486	1.445
$^{80}SeO_2$	111.90	1.000	**4.022**	**5.181**
$^{80}SePO$	126.88	1.000	0.777	0.635
$^{80}SePO_2$	142.88	1.000	0.779	0.538
^{114}CdO	129.90	1.000	1.231	1.043
$(C_8H_{17})_2P_2O_5$+^{114}Cd	482.07	1.000	0.695	0.432

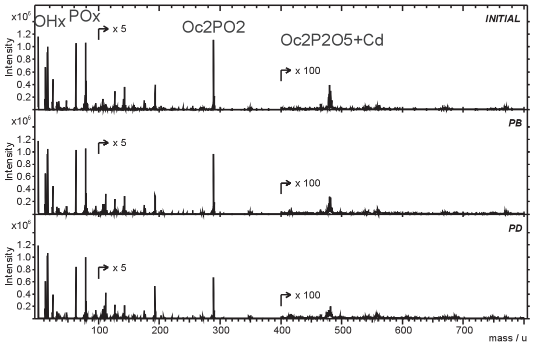

Fig. 5-1 Negative ion ToF-SIMS spectra from CdSe nanocrystals thin films, in initial, PB and PD states.
Overview in the mass range of *m/z* 0-800.

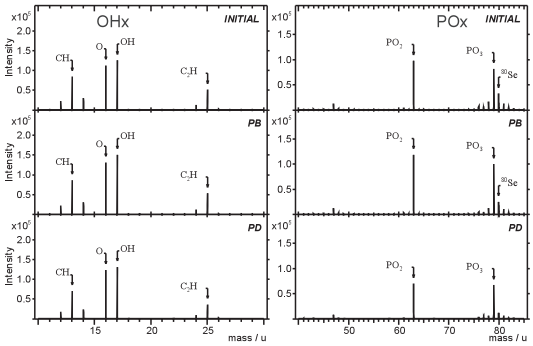

Fig. 5-2 Negative ion ToF-SIMS spectra from CdSe nanocrystals thin films, in initial, PB and PD states.
Zoomed view of OH_x^- and PO_x^- regions.

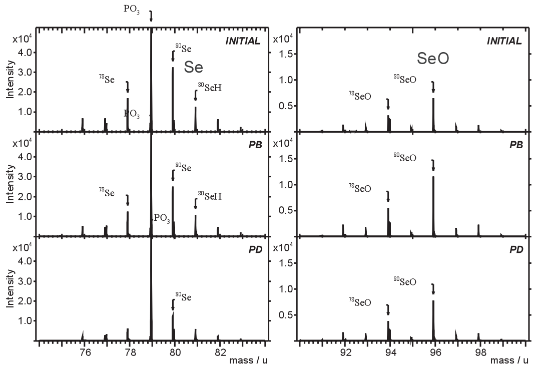

Fig. 5-3 Negative ion ToF-SIMS spectra from CdSe nanocrystals thin films, in initial, PB and PD states.
Zoomed view of Se^- and SeO^- regions.

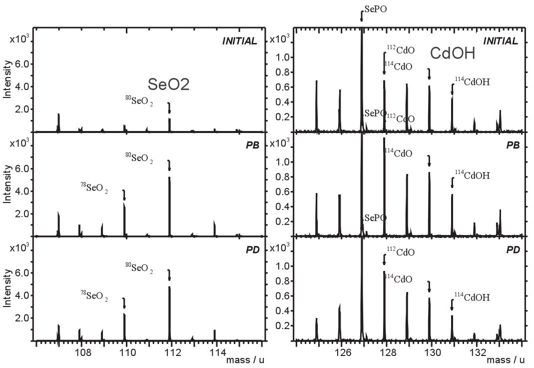

Fig. 5-4 Negative ion ToF-SIMS spectra from CdSe nanocrystals thin films, in initial, PB and PD states.
Zoomed view of SeO_2^- and $CdOH_x^-$ regions.

4. Correlation between surface chemical structure changes and optical properties

4.1. Chemical structure changes

Based on XPS and ToF-SIMS results, the changes in the surface chemical structure of TOPO-capped CdSe nanocrystals are proposed as follows: In the initial state, TOPO binds to Cd site, which is deduced from the presence of TOPO+Cd cluster ions. After the short laser irradiation, a part of TOPO molecules are excited, described TOPO*, and slightly positive charged. Then TOPO* migrates on the surface from Cd site to Se site. This process is deduced from the observation of the characteristic enhancement of TOPO molecular ion peaks, and the appearance of the peaks of its dimer ions and TOPO+Se cluster ions in the PB state. The prolonged laser irradiation induces the further progress in the oxidation of surface Se and the decomposition of TOPO*, which is followed by TOP and SeO_2 desorption.

4.2. Optical properties

In the PB state, increase in PL intensity and blue shift of the peak position are observed. Enhanced PL intensity is explained to be due to the increase of the degree of surface nonradiative recombination site passivating by the rearrangement of the organic ligand TOPO*. Gradual blue shift of the peak position is attributed to the shrinkage of CdSe nanocrystals by desorption of SeO_2 as a result of the Se oxidation.

5. Comparison of oxidation index for Cd and Se extracted by XPS and ToF-SIMS

In order to prove the usefulness of ToF-SIMS as a tool for chemical state analysis of elements, oxidation index for Cd and Se extracted from XPS and the results of ToF-SIMS are comparatively discussed below.

5.1. Oxidation index for Cd

It is known that core-level spectra of Cd do not show detectable chemical shifts among the various chemical states. This is compatible with the present results; there was no significant change in Cd 3d and Cd MNN spectra, except for the slight energy shift toward the lower kinetic energy. Even when the chemical shifts in XPS spectra are small, further information on the chemical state may be obtained from Auger parameter (AP) [5], whose concept was introduced by Wagner. The AP for Cd is estimated from the Cd $3d_{5/2}$ and Cd $M_4N_{45}N_{45}$ peaks in XPS spectra, using the following equation.

$$AP = BE\,(Cd\ 3d_{5/2}) + KE\,(Cd\ M_4N_{45}N_{45})$$

The estimated AP values are shown in Table 4 and Fig.6(a). With increasing laser irradiation time, the AP slightly decreases, however, the observed change in AP is too small to identify the progress of oxidation. In short, the chemical state change of Cd cannot be detected in XPS even if the AP values are calculated.

As mentioned above, the organic ligand TOPO is likely to adsorb on the Cd sites with the O end, which leads to the chemical interaction between Cd and O. After laser irradiation, some TOPO migrate on the surface from Cd sites to Se sites in the PB and PD state, which may allow water to attack the bare Cd sites. However, it is difficult to prove the interaction between water and Cd from XPS as discussed above.

In contrast with XPS, there is an unambiguous sign of Cd-water interaction in positive ion ToF-SIMS spectra. With increasing laser irradiation time, the intensity ratio of CdOH / Cd clearly increases, as shown in Fig.6(a). This result indicates that the surface species covered on the Cd sites changed from TOPO to water after laser irradiation.

One possible reason for the difference between XPS and ToF-SIMS results about the sensitivity for changes in Cd chemical environment is the difference in the information depths. It should be taken into account that the information depth of ToF-SIMS is smaller than that of XPS [7]. It is considered that the chemical environment changes occur only at the outermost surface, and in this case ToF-SIMS should have the advantage of sensitivity.

Table 4. Cd Auger parameter obtained from CdSe nanocrystals thin films, and reference values [5,6].

Sample	Cd $3d_{5/2}$ (BE,eV)	Cd $M_4N_{45}N_{45}$ (KE,eV)	AP (eV)	ΔAP (eV)
Initial	404.8	381.2	786.0	0.0
PB	405.0	381.0	785.9	-0.1
PD	404.9	380.7	785.6	-0.4
Cd [5]	405.0	384.0	789.0	0.0
CdO [5]	404.2	382.4	786.6	-2.4
$Cd(OH)_2$[5]	405.1	380.0	785.1	-3.9
Cd[6]	405.0	383.8	788.8	0.0
CdO [6]	405.2	382.2	787.4	-1.4
CdSe [6]	405.3	381.4	786.7	-2.1
CdS [6]	405.3	381.1	786.4	-2.4
CdF_2 [6]	405.9	378.8	784.7	-4.1

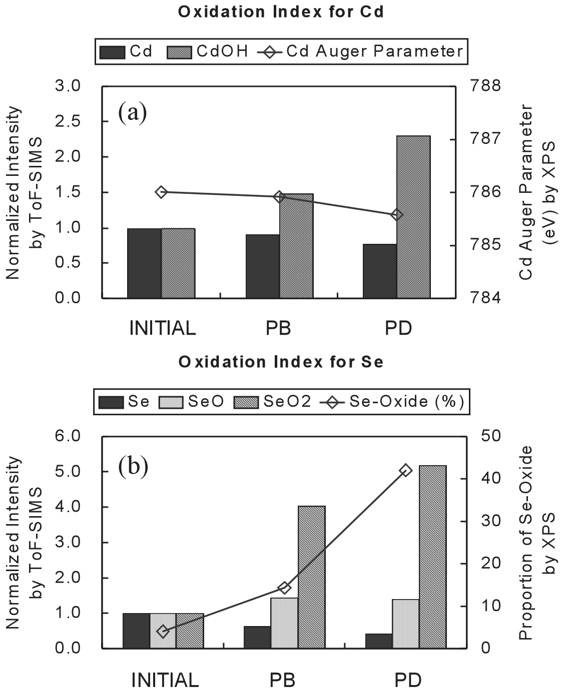

Fig. 6 Comparison of oxidation index for Cd and Se, obtained by XPS and ToF-SIMS.

5.2. Oxidation Index for Se

Compared with Cd, drastical change was induced by laser irradiation in the Se 3d XPS spectra, which gives much direct information on the chemical state change. With increasing laser irradiation time, a new peak arising from Se oxide appeared at 59 eV, which is well separated from the Cd-Se peak remaining at 54 eV. In this case, we can easily estimate the proportion of the number of Se atoms in each chemical state from XPS spectra. The variation in the proportion of Se oxide is shown in Fig.6(b), which gives quantitative information on the proportion of each.

Unambiguous sign of Se oxidation is also obtained from negative ion ToF-SIMS spectra. With increasing laser irradiation time, the intensity ratio of SeO_2 / SeO and SeO / Se increases step by step, as shown in Fig.6(b). These changes clearly indicate the progress in surface oxidation of Se. Nevertheless, it is not easy to extract the quantitative information on the chemical state of elements from ToF-SIMS spectra.

6. Summary

We demonstrate that the complementary information can be obtained on the changes in surface chemical structure of TOPO-capped CdSe nanocrystals by comparative use of XPS and ToF-SIMS. Based on the results obtained, the changes in the surface chemical structure are proposed as follows:

1) In the initial state, TOPO molecules are likely to bind to the Cd sites, which is proved by the detection of TOPO+Cd cluster ions.

2) In the PB state, where PL intensity increases after the short laser irradiation, a part of TOPO molecules are excited, described TOPO*, and slightly positively charged. Then some TOPO* migrate on the surface from Cd sites to Se sites, forming TOPO*+Se complex.

3) In the PD state, where PL intensity gradually decreases after the long duration of laser irradiation, TOPO*+Se complexes are decomposed, which leads to the desorption of TOP and SeO_2.

XPS can provide the quantitative information on the elemental composition and the chemical state of elements in the surface region. However, there are some limitations to distinguish one chemical state from others or to characterize the chemical structure of organic molecules. ToF-SIMS can give not only the qualitative information on the chemical state of elements but also the chemical structure of surface organic molecules. For example, ability for detection of the cluster ions between organic ligand and substrate element can provide the direct evidence of the chemical interaction. It can be concluded that the combination of XPS and ToF-SIMS is a very powerful method for microscopic chemical analysis for various surfaces.

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