Local environment surrounding S and Cd in CdS:O thin film photovoltaic materials probed by x-ray absorption fine structures

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Local environments surrounding Cd and S in CdS:O thin films have been determined using extended x-ray absorption fine structure (EXAFS) and near-edge x-ray absorption fine structure (NEXAFS). As indicated by the Cd EXAFS, Cd atoms remain predominantly bonded with S. The S EXAFS and NEXAFS clearly demonstrate the presence of S–O bonds. The oxygen atoms actually combine with S to form SO$_3$ and SO$_4$ complexes. Combined with the transmission electron micrograph, these x-ray results suggest formation of oxygen-free CdS nanocrystals and provide an unambiguous explanation for the mystery of increased band gap that appears to violate the band anticrossing model. © 2006 American Institute of Physics. [DOI: 10.1063/1.2356995]

The CdS/CdTe heterojunctions have shown many promising properties in photovoltaic applications such as high light-conversion efficiency, enhanced short-wavelength response, low series resistance, stability, and high radiation tolerance. Further improvement of this material is therefore considered to be of great importance for developing next-generation photovoltaic technologies. The band gap of the n-type CdS window can play an important role in affecting the overall performance of the heterojunction as a photovoltaic device. According to the band anticrossing model, incorporation of highly electronegative O atoms into the II–VI CdS host should effectively lower the measured band gap of the resultant material due to splitting of the conduction band. However, a recent experimental work has shown that O content in CdS films grown by rf sputtering can instead increase the band gap of CdS.

For a reasonable explanation of the band gap increase that seems to violate the well-established band anticrossing model, detailed structural information on the location of O impurity atoms in the sample appears to be a crucially important prerequisite. To this end, the short-range-order extended x-ray absorption fine structure (EXAFS) method is uniquely suitable for probing the impurity atoms that do not have long-range structural order in the host. However, since the glass substrate used in the growth of thin film solar cell contains plenty of oxygen atoms, it is difficult to measure the O EXAFS exclusively from the CdS:O film without being affected by the glass substrate. In the present work, we have instead probed the local chemical environment around constituent Cd and S atoms using Cd K- and S K-edge EXAFS, as well as S K-edge near-edge x-ray absorption fine structure (NEXAFS).

Samples of CdS:O were grown by rf sputtering with O/Ar ratios of 0% (S397), 2% (S399), and 5% (S402) on glass substrate at room temperature (~20 °C). Formation of nanosized particles in the samples is revealed by transmission electron micrograph (TEM); the TEM of the 2% sample is shown in Fig. 1(a) as an example. The grain size in the 2% sample is about a few tens of angstroms, which is one order of magnitude smaller than the poly-CdS film. The electron diffraction pattern demonstrated in Fig. 1(b) for the 2% sample also shows typical characters of a predominantly nanocrystal sample. The band gaps of samples sputter grown with O$_2$/Ar ratios of 0%, 2%, and 5% were measured using optical methods to be 2.42, 2.65, and 3.17 eV, and O concentration using x-ray photoemission spectroscopy to be 4.35%, 8.66%, and 22.73%, respectively.

The Cd K-edge EXAFS measurements were performed at beamline X3B1 at National Synchrotron Light Source at Brookhaven National Laboratory. A conventional fluorescence detection mode is adopted using a single element Si(Li) detector to collect the fluorescence photons from the samples. A well-known data reduction program was used to extract the EXAFS $\chi$ functions from the raw experimental data. The $\chi$ functions of the three samples under investigation are then Fourier transformed into real space plotted as fine lines in Fig. 2. Local structural parameters were quantitatively extracted from the $\chi$ functions using an improved curve-fitting procedure and are listed in Table I. The S K-edge NEXAF and EXAFS spectra were also measured in fluorescence mode at beamline BL15B at National Synchrotron Radiation Research Center in Taiwan using a Lytle fluorescence yield detector. The S K-edge NEXAFS data for all three samples are plotted together in Fig. 3. Following a

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FIG. 1. TEM and electron diffraction patterns of CdS film deposited in 2% O$_2$/Ar.
similar procedure adopted in analyzing the Cd EXAFS data, the Fourier transform of S K-edge EXAFS was obtained as plotted in Fig. 4 and the parameters obtained from curve fitting are listed in Table II.

As shown in Fig. 2 and Table I, the Cd atoms are coordinated by S nearest neighboring atoms. The Cd–S bond length, however, is found to decrease with increasing O content in the sample. As the O content in the sample increases, the coordination number of the nearest S shell around Cd decreases and the local disorder increases. The Cd EXAFS data show no sign of Cd–O bonds in the samples.

As we can see in Fig. 3, the S K-edge NEXAFS data for the sample with 0% O/Ar ratio show a typical CdS spectrum.5,6 However, the data for samples with 2% and 5% O/Ar ratio are largely different from those of the 0% sample. Two additional peaks located at 2477.2 and 2481.6 eV with increasing peak height as the O/Ar ratio increases are attributed to contributions from SO3 and SO4 complexes,7 The existence of S–O bonding is also revealed by the S K-edge EXAFS results. As demonstrated in Fig. 4 and Table II, in addition to the Cd near neighboring shell of S in CdS, O near neighboring atoms also appear in the two oxygen-containing samples, indicating formation of S–O compounds, while the undoped sample remains predominantly CdS. The results of Cd and S x-ray absorption fine structures (including NEXAFS and EXAFS) thus clearly demonstrate that Cd atoms only exist in the CdS compound while S atoms are present in both the CdS and certain S–O compounds including most likely SO3 and SO4 complexes. Moreover, the decreasing coordination number of the nearest S shell around Cd as the O concentration increases indicates that CdS in the oxygen-containing samples are in the form of nanoparticles with decreasing particle size.

Based on the TEM and x-ray results, it appears that as O content is added in the rf-sputtering growth of CdS, part of the S atoms can combine with O to form SO3 and SO4 complexes while other S atoms form CdS nanoparticles with Cd atoms. The increased band gap in the CdS:O samples may have arisen from the quantum confinement effect of nanocrystal CdS. The decreasing size of CdS nanoparticles that leads to increasing quantum confinement effect is also revealed by the decreasing coordination number of S neighboring shell around Cd as the O/Ar ratio increases. In conclusion, our XAFS results have experimentally demonstrated a detailed mechanism of the formation of oxygen-free CdS nanocrystals and therefore addressed the question of the absence of band anticrossing effect in oxygen-containing CdS thin films grown by rf sputtering.

### Table I. Parameters of local structure around Cd atoms obtained from curve fitting of the Cd K-edge EXAFS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Neighboring atom</th>
<th>N</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\Delta E$ (eV)</th>
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<tbody>
<tr>
<td>S397</td>
<td>S</td>
<td>4</td>
<td>2.47±0.01</td>
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<tr>
<td>S399</td>
<td>S</td>
<td>3.6±0.3</td>
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<td>6±1</td>
<td>1±1</td>
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<tr>
<td>S402</td>
<td>S</td>
<td>3.5±0.4</td>
<td>2.45±0.01</td>
<td>11±1</td>
<td>−4±3</td>
</tr>
</tbody>
</table>

### Table II. Parameters of local structure around S atoms obtained from curve fitting of the S K-edge EXAFS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Neighboring atom</th>
<th>N</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
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<td>S397</td>
<td>Cd</td>
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<td>2.49±0.01</td>
<td>3±1</td>
<td>2±1</td>
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</table>


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