Investigation of interface morphology and composition mixing in CdTe/CdS heterojunction photovoltaic materials using synchrotron radiation

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The interface microstructure in thin film photovoltaic materials is an important problem which can severely affect the light-conversion efficiency and stability of heterojunction solar cells. This is a long-standing fundamental problem, but has not been studied in the past by effective probing methods. In the present experiment, the interfacial roughness, correlation lengths of interface height fluctuations, effects of heat treatment, and diffusion of Te atoms across the heterojunction interface have been investigated by means of grazing incidence x-ray scattering and angular dependence of x-ray fluorescence using synchrotron radiation. We thus demonstrate that these x-ray techniques can provide a powerful tool for nondestructive characterization of the interfacial roughness and intermixing of selected atomic species in heterojunction photovoltaic materials.

I. INTRODUCTION

Advances in photovoltaics are crucially dependent on the fundamental understanding of physical properties of the solar cell materials. Among a large variety of photovoltaic (PV) materials, semiconductor layered structures have recently shown great promise to be the most efficient system for sunlight energy conversion. Of particular interest are the direct gap semiconductor heterojunctions, e.g., CdTe and CuInSe₂, which show many useful advantages such as enhanced short wavelength response, low series resistance, stability, and high radiation tolerance. At the present time, however, many fundamental problems about the physical mechanisms concerning the performance of PV heterojunctions still remain poorly understood. The lack of understanding of the layered-material morphology, especially in the built-in internal electric field region around the interface, has hindered progress in the development of PV heterojunctions for large-scale applications.

There are many problems concerning the morphology of the interface when a heterojunction is formed between two dissimilar semiconductors, e.g., the inevitable presence of interfacial roughness, the local strain as a result of lattice mismatch, and intermixing of atoms across the interface. Since these structural imperfections take place in the most important internal field region, all can cause local traps and undesirable scattering of electrons, thereby limiting the mobility or lifetime of the excess minority charge carriers. Due partially to the lack of effective tools for probing the microscopic structures of buried interfaces in layered structures, these important issues have thus far not been fully addressed by the PV research community.

The advent of polarized, tunable, high-intensity x rays from synchrotron radiation has now made it possible to investigate detailed microscopic structures in ways which were not possible before. Of particular interest is the interaction of high-intensity short-wavelength x rays with structures on the nanometer scale. Through a control of the incidence angle and wavelength, the penetration depth as well as the element selectivity of the probing x ray can be varied. This capability is of particular interest for studying layered structures of compound semiconductors such as heterostructures and superlattices, but it has hitherto not been applied to the investigation of solar cell materials. Studies of PV heterojunctions using the powerful tools of x rays from synchrotron radiation would seem highly desirable.

The natively p-type CdTe has a direct gap of 1.45 eV at room temperature, with strong ionicity and a high absorption coefficient. When coupled with the n-type window partner CdS, this heterojunction has already shown a high efficiency of approximately 15.8% in the laboratory. These useful PV characteristics also make this heterojunction potentially a strong candidate for an important “next generation” solar cell material. On the other hand, the large (~10%) lattice mismatch between CdTe and CdS is expected to cause a large interfacial roughness. Further, diffusion of Te to the CdS layer when the material is subjected to heat treatment can result in a blurred interface. Since these microstructures occur in the most important internal field region around the CdTe/CdS interface, they can be detrimental to the mobility of the excess charge carriers and therefore the light conversion efficiency of the solar cell device.

In the present experiment, grazing incidence x-ray scattering (GIXS) and angular dependence of x-ray fluorescence (ADXRF) techniques have been applied for the first time to a study of the CdTe/CdS heterojunctions. As more work is still in progress, the microstructural information obtained thus far has already demonstrated that these synchrotron radiation techniques are very useful tools for the study of heterojunc-
The Born approximation can be applied to investigate the efficiency for one-sun illumination. The typical CdTe cell has a superstrate structure with soda-lime glass/combination of the x-ray diffuse scattering data with model calculations, the parameters \( \sigma^* s, \xi \parallel, \xi \perp \), and \( h \) can be determined. It should also be noted that diffuse scattering can also contribute to Bragg diffraction peaks (with the spacing of interfaces playing the role of atomic spacing in the conventional diffraction) similar to the Bragg peaks usually observed in specular reflection. A quantitative measurement of the diffuse scattering contribution is therefore necessary in order to obtain the true specular reflectivity.

In our experiments, the specular reflectivity is obtained by varying the grazing incidence angle while keeping the detector at an exit angle equal to the incidence angle, the photon momentum transfer is always perpendicular to the interface in this scan \( q_x = 0, \) and \( q_z \) is proportional to the grazing angle. In addition, both the longitudinal diffuse scattering (LDS) and transverse diffuse scattering (TDS) components are measured. The LDS data are taken by setting the x-ray detector at an exit angle different from the direction of specular reflection while varying the incidence angle, thereby obtaining structural information with a nonzero component of photon momentum transfer parallel to the interfaces; thus LDS allows \( \xi \parallel \) to be determined. In the measurements of TDS, the sample under study is rocked through the configuration of specular reflection while maintaining both the incident beam and detector at fixed directions (this is also known as \( \omega \) scan); for grazing incidence, this arrangement provides structural information from changing the photon momentum transfer \( q_z \parallel \) parallel to the interface with an essentially constant \( q_x \). These scattering experiments can offer a wealth of useful information about vertical and lateral correlations between interfacial height fluctuations.

In the treatment of x-ray fluorescence yield (FY) we neglect the incoherent scattering contributions and assume that x-ray photons lose all energy via excitation of the atoms in the material to different states. The small energy losses to Compton effect, phonon scattering, etc., are all neglected. Thus, the FY intensity is proportional to the energy absorbed in the layers as well as the density profile of fluorescent atoms, and it can be written as:

\[
I_{FY} \propto \int_0^D dz \left( \frac{dS_z}{dz} \right) \rho_{FA}(z),
\]

where \( S_z \) is the \( z \) component (perpendicular to the interfaces) of the Poynting vector, \( \rho_{FA}(z) \) is the density profile of the fluorescent atoms in the \( z \) direction, and \( D \) is the x-ray penetration depth. In an ADXRF experiment, the x-ray penetration depth is changed by varying the incidence angle, the results can provide useful information about the compositional depth profile normal to the surface pertaining to a selected atomic species in the layer material.

B. Samples

Heterojunction samples used in the present experiment were prepared by rf planar magnetron sputtering of the thin film materials. The film deposition conditions were the same as reported in Ref. 16 which has yielded cells with 11.6% efficiency for one-sun illumination. The typical CdTe cell has a superstrate structure with soda-lime glass/
SnO$_2$:F/CdS/CdTe/metal. We call this ordering of the semiconductors the "normal" structure. The CdS and CdTe thicknesses are typically 0.1–0.2 μm and 2–4 μm, respectively. For the present work, very thin films (bilayers of CdS and CdTe) were sputtered directly onto Corning 7059 glass to take advantage of the smoother surface. A normal (CdTe on CdS, sample number: UB-1) and an inverted (CdS on CdTe, UB-2) bilayer heterojunction were investigated for comparison of the interfacial roughness. Further, for a comparison of the interface morphology of CdS or CdTe grown alone on glass, two single layer samples of CdS/glass (UB-3) and CdTe/glass (UB-4) were also studied. The nominal layer thickness for CdTe and CdS layers in these four samples was approximately 20±5 nm.

In addition, for an investigation of Te mixing across the CdTe/CdS interface and the effect of thermal annealing, the sample UB-2 and two similar samples which had been subjected to thermal annealing at 330 and 358 °C for 30 min, respectively, were studied using the ADXRF technique.

III. RESULTS AND DISCUSSION

The GIXS technique was used to determine the individual layer thickness and to investigate the surface and interfacial roughness parameters as well as the correlation lengths in the heterojunction samples. For a study of diffusion of Te atoms from CdTe into the CdS layer in the heterojunction, the ADXRF technique was employed. The results are presented separately in the following.

A. Grazing incidence x-ray scattering (GIXS) measurements

Typical specular reflectivity and LDS data are shown in Fig. 1. It is evident that the LDS (lines) exhibits oscillations similar to the specular reflectivity (open circles), indicating that the interfaces in each sample are correlated. However, pronounced oscillations appear only in the low $q_z$ region, suggesting a large rms roughness in these samples. The oscillations are weaker in the bilayer junctions as compared to the single layer samples, hence the interfaces are degraded when more layers are added. The LDS oscillations are very weak for the bilayer samples, suggesting that the correlation lengths are short in the normal direction. Detailed curve-fitting analysis of the LDS data shows that the cross-correlation lengths in the bilayer samples UB-1 and UB-2 are 200 and 240 Å, respectively, comparable to the individual layer thickness, consistent with the fact of rough and random fluctuations on the CdTe/CdS interfaces (see Table I).

Results of curve-fitting analysis of the specular reflectivity are shown in Figs. 2 and 3. The corrected true specular components (open circles) are obtained after subtracting out the diffuse scattering contributions. The solid curve in each plot is a theoretical fit using the model discussed in the previous section. We find the theoretical calculation in excellent agreement with the experimental data, reproducing practically all the oscillation amplitudes and frequencies. Figure 2 shows the specular reflectivity along with theoretical calculations for CdS and CdTe single layers grown on glass substrates. Both the surface and interfacial rms roughness parameters are similar for CdS and CdTe single layers grown on glass, indicating that CdS and CdTe are equally compatible with Corning 7059 glass substrates.

Curve-fitting results of specular reflectivity for the normal (CdTe on CdS, #UB-1) and inverted (CdS on CdTe, #UB-2) bilayer samples are shown in Fig. 3. The interfacial roughness seems to be similar in these junctions. By a comparison of Figs. 2 and 3, it can be concluded that the interfacial roughness between CdTe and CdS is mainly determined by the top surface morphology of the bottom layer grown on glass. Hence, a smooth surface finish of the first layer is a necessary condition for preparing high quality heterojunction solar cells with planar interfaces.

The TDS results are shown in Fig. 4. The TDS is sensitive to the lateral (in-plane) fluctuations, characterized by a lateral-correlation length $\xi_l$. The theoretical fits based on Eq. (1) are in very good agreement with our TDS data. Quantitative results of our curve-fitting analysis, from which we have determined the individual film thickness, interfacial roughness parameters, and correlation lengths from the data of specular reflectivity, LDS and TDS, are summarized in Table I. The overall quality of surface and interfaces is similar in the normal and inverted junctions, except that the UB-1 normal junction seems to show a slightly higher lateral correlation and lower vertical correlation than the inverted junction (UB-2).

B. Angular dependence of x-ray fluorescence (ADXRF) measurements

Intermixing of atoms between constituent layers is a fundamental problem of vital importance for heterojunction PV
materials. Diffusion of different atomic species across the interface can give rise to a compositional/structural blurred boundary between the layers. This can lead to undesirable scattering and cause additional traps for the charge carriers around the interface, both are probably detrimental to the light-conversion efficiency of the solar cells. On the other hand it has been speculated that interdiffusion may also serve to relieve some of the interfacial strain and produce some beneficial band bending. Furthermore, it is likely that the interdiffusion will proceed faster along grain boundaries than in the bulk of the grains, thus leading to an interface roughening. In the present experiment, Te diffusion across the CdS/CdTe interface in an inverted-junction sample UB-2 has been investigated by using the ADXRF technique.

The x-ray fluorescence output for a given field distribution at a fixed incidence angle can offer information on the concentration depth profile of atoms which produce the fluorescence yield [see Eq. (2)]. By varying the probing depth of x rays through changes of the incidence angle, relative variations in the content of a specific atomic species around the interface can therefore be compared. Using this ADXRF technique, we have also investigated the effect of thermal annealing on the inverted junction UB-2.

To provide a simple picture of the overall angular variation of Te fluorescence yield for this inverted junction, the x-ray flux distribution inside the sample for various incidence angles was calculated at first. At a given incidence angle, the spatial variation of the field intensity is thus obtained, and the characteristic length of intensity decay in the material is determined as the penetration depth for that particular incidence angle. By a given penetration depth of the x-ray beam (corresponding to a specific incidence angle), the total intensity of x-ray fluorescence yield can be obtained.

### Table I. Structural parameters of heterojunctions determined from GIXS measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characteristic</th>
<th>$D_1$ (Å)</th>
<th>$D_2$ (Å)</th>
<th>$s_0$ (Å)</th>
<th>$s_1$ (Å)</th>
<th>$s_2$ (Å)</th>
<th>$h$</th>
<th>$\xi_l$ (Å)</th>
<th>$\xi_c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB-1</td>
<td>CdTe/CdS/glass</td>
<td>183±10</td>
<td>159±12</td>
<td>22±6</td>
<td>16±10</td>
<td>5±0.5</td>
<td>0.15</td>
<td>548</td>
<td>200</td>
</tr>
<tr>
<td>UB-2</td>
<td>CdS/CdTe/glass</td>
<td>255±10</td>
<td>270±10</td>
<td>17±9</td>
<td>14±10</td>
<td>6±0.5</td>
<td>0.2</td>
<td>424</td>
<td>240</td>
</tr>
<tr>
<td>UB-3</td>
<td>CdS/glass</td>
<td>292±5</td>
<td>...</td>
<td>17±5</td>
<td>...</td>
<td>5±0.5</td>
<td>0.23</td>
<td>629</td>
<td>440</td>
</tr>
<tr>
<td>UB-4</td>
<td>CdTe/glass</td>
<td>...</td>
<td>258±6</td>
<td>15±5</td>
<td>...</td>
<td>5±0.6</td>
<td>0.3</td>
<td>532</td>
<td>420</td>
</tr>
</tbody>
</table>

**FIG. 2.** Corrected true specular reflectivity vs $q_z$ for two single layer samples grown on glass substrates.

**FIG. 3.** Corrected true specular reflectivity vs $q_z$ for normal and inverted bilayer samples.
by integration in accordance with Eq. (2). The calculated photon flux spatial distribution in sample UB-2 is shown in Fig. 5 for various grazing incidence angles $\theta$ below ($\theta = 0.03^\circ$, 0.05$^\circ$, and 0.073$^\circ$) and above ($\theta = 0.077^\circ$, 0.08$^\circ$, and 0.1$^\circ$) the critical angle ($\theta_c = 0.075^\circ$) at 31.9 keV, the energy used in our ADXRF measurements. In this calculation, structural parameters obtained earlier from our specular reflectivity data were used and the value of critical angle was determined self-consistently by using this procedure. The oscillations of flux distribution are caused by interference between the transmitted and reflected x-ray fields inside the layered material. Based on the flux distribution shown in Fig. 5, the penetration depth of x rays in this heterojunction as a function of the incidence angle is shown in Fig. 6. This plot can be used to convert the incidence angle to the corresponding x-ray penetration depth for investigating the depth profile of Te atoms around the interface.

The x-ray fluorescence yield was measured by using a Si(Li) energy-dispersive detector with the incident x-ray energy tuned to 31.9 keV (slightly above the K-edge binding energy 31.8 keV for Te) in the ADXRF measurements, so that fluorescence from both Te and Cd atoms can be excited. The measured FY is plotted as a function of yield energy at various incidence angles in Fig. 7. Two FY peaks shown in this figure are clearly identified as arising from Cd K$\beta$ at 26.096 keV and Te K$\alpha$ at 27.472 keV, respectively. The intensities of these peaks are normalized with respect to that of Cd K$\alpha$ at 23.174 keV (not shown in this plot). Since the top layer CdS has a lower critical angle detected first by the incident x-ray beam, and Cd is present in both CdS and CdTe layers, the intensity of Cd K$\alpha$ and Cd K$\beta$ FY therefore changes gradually with the penetration depth as the grazing incidence angle is increased. However, the FY intensity of Te K$\alpha$ at 27.472 keV varies sensitively with the in-
incident angle or the probing depth of the x-ray beam, depending on the depth profile of the Te atoms.

The general shape of the angular dependence of Te Kα FY intensity appears similar to the angular dependence of penetration depth in the CdTe/CdS heterojunction (see Fig. 6), suggesting at first sight that the effect on angular variation of Te Kα FY might mainly arise from the changes in the x-ray probing depth. For a preliminary comparison, we have calculated the Te Kα FY intensity from Fig. 6 and Eq. (2) using a simplified assumption of an abrupt CdTe/CdS interface, i.e., without diffusion of Te across the boundary or a step-function Te density profile. This calculation is shown in Fig. 8 compared with the measured FY intensity deduced from Fig. 7 for various penetration depths corresponding to incidence angles below and near the critical angle. Deviations of the FY data from this theoretical calculation clearly shows that the Te density profile at the interface is not a simple step-function; the effect of Te diffusion across the CdTe/CdS interface cannot be neglected. This result demonstrates that ADXRF is a convenient method for nondestructive characterization of the intermixing of selected atomic species around the interface.

Based on the ADXRF method, we have also investigated the effect of thermal annealing on Te diffusion around the interface by using the angular dependence of Te Kα FY. The total FY intensity is obtained by curve-fitting the entire measured FY curve and by integration. The normalized angular dependence of total intensity of Te Kα FY is shown in Fig. 9 for three samples prepared under different anneal conditions. Without a detailed theory of the ADXRF at the present time, a quantitative comparison of these data is made by an empirical approach. The data points can be fitted reasonably well with an arctangent function as follows:

\[ y = y_0 + A \tan^{-1}\left(\frac{2(x-x_0)}{W}\right), \tag{3} \]

where \( x \) and \( W \) are directly proportional to the incidence angle; \( y \) represents the ratio of Te Kα to Cd Kα fluorescence yield; \( y_0 \) is a background largely due to Te fluorescence from the edges of the sample or from possibly minute Te contamination in the CdS layer caused by sample handling. The parameters \( A \), \( x_0 \), and \( W \) represent the magnitude, midpoint of...
the steplike rise, and a characteristic width of the FY with increasing incidence angle, respectively. The results of the arctangent fits are given in Table II.

The parameters $x_0$ and $W$ can be used to characterize the mixing of Te about the CdTe/CdS interface. For an abrupt interface, the width $W$ should be zero, and no trace of Te should be found in CdS. Diffusion of Te into the CdS layer could result in a broadened distribution of Te about the interface, with a lower value of $x_0$ and a larger width $W$ compared to the abrupt interface. A lower value of $x_0$ represents the fact that the incident x-ray beam senses the presence of Te atoms at a shallower depth (lower incidence angle) before its penetration depth reaches the CdTe/CdS interface.

From Fig. 9, we can see that the overall data points of annealed samples are higher than those of the unannealed sample. Also, the position of the steplike rise for the annealed samples is at smaller incidence angles than the unannealed sample. The midpoints of the arctangent rise in the annealed samples are closer to the sample surface compared to that of the unannealed sample. Also, annealing at 358 °C results in a broadened width of Te distribution. These results indicate that annealing has caused significant mixing of Te between the CdS and CdTe layers. While more work is in progress, this result demonstrates that the ADXRF technique is well suited for investigating the intermixing of specific atomic species across the boundary between different layers in the heterojunction material.

### IV. CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

Synchrotron radiation techniques of GIXS and ADXRF have been utilized to investigate the interface morphology of CdTe/CdS heterojunction solar cell materials. These methods are nondestructive, and uniquely suited for studying the buried interfaces in layered structures. The scattering results allow accurate determination of the individual layer thickness and provide useful information on the interfacial roughness and correlation lengths of interface height fluctuations. The fluorescence data provide a quantitative display of interface broadening caused by Te diffusion across the CdTe/CdS junction interface, this is useful for comparing the changes in the interface width resulting from thermal annealing. A more detailed investigation of the annealing effect on Te distribution is in progress, by using the techniques of ADXRF and anomalous x-ray scattering.\(^1\)\(^8\)–\(^2\)\(^0\)

Since these are only the first-time results, it would seem natural that some other measurements could be carried out to obtain further useful information of the PV materials immediately following the approach of the present experiment. In general, these x-ray techniques are especially useful for clarifying the generic properties of interfaces in the heterojunctions. The interface microstructure, e.g., roughness and compositional inhomogeneities, can give rise to traps and hinder the excess carriers to traverse through the internal field. Also, irregular top surface morphology could cause loss of incident power. Thermal annealing and other activation processes could induce changes of microstructures around the interfaces. With the help of the x-ray techniques, it has now become possible to pursue nondestructively detailed quantitative evaluation of these structural problems and make a detailed comparison with other experimental methods such as Rutherford backscattering\(^2\)\(^1\) currently available in the field for a better physical understanding of the PV materials. An improvement of the interface microstructure might raise the hope to reach a new world record of the conversion efficiency in thin film polycrystalline solar cells.

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