Effect of Intense Magnetic Field on Electro-deposited Thin Film of CdTe

T. Kozuka, K. Shimomai, T. Kenjo, M. Kawahara

Abstract

CdTe semi-conductor is expected as solar cell materials. Electro-deposition process of CdTe is considered advantageous because of its superior cost performance, and large grain size structure is preferable for higher energy conversion. In this paper, an innovative method using intense magnetic field is proposed, where CdTe grains with large size are obtained.

Magnetic field has a function of crystal orientation due to anisotropy of magnetic susceptibility. In the experiments, two steps of electro-deposition process and successive annealing process were conducted. In the first step, Te or Cd thin film was deposited under intense magnetic field to obtain highly oriented structure. Next, CdTe film was deposited onto the first layer. After the second deposition process, textures of CdTe grains were aligned because of epitaxial deposition. In the annealing process, grain growth occurs very actively, because the aligned structure is advantageous for the growth of large grains.

Finally, the grain size of CdTe is evaluated by scherrer’s equation, and the possibility of obtaining larger size of CdTe grains is shown in the case of CdTe film on Te film.

Introduction

Recently, in order to suppress global warming, various alternative energies without fossil fuel are researched, developed and discussed. CdTe semi-conductor film has been expected as a solar cell material, because of its high-energy conversion ratio in theory. However, the actual conversion ratio of CdTe film is still low, which suggests there is much room to study about the structure, the electrical property, and the processing of CdTe film for obtaining higher conversion ratio[1,2]. Especially, grain size control is very important, because large grain size is advantageous for the conversion ratio.

Magnetic field has a function of crystal orientation due to the anisotropy of magnetic susceptibility. It is expected that a series of a deposition process and successive heat treatment process can produce large grains because the grain boundary between well oriented crystals is easy to disappear and easy to form large grain structure. However CdTe crystal has cubic structure so that magnetic field cannot affect the crystal orientation.

In this study, a new method obtaining large grains is proposed, where two electrodeposition processes and a successive annealing process are combined. A base layer of Cd or Te is deposited under intense magnetic field preliminary. Cd or Te has hexagonal structure and has anisotropy of magnetic susceptibility, and the deposited grains can be oriented[3]. Next to the first layer, CdTe is deposited epitaxially, where the alignment of the textures of CdTe grains is expected. In the annealing process, the boundaries between the grains with almost same texture are easy to disappear so each deposited grain can grow relatively larger.

In this paper, the experimental procedure and the results about the size of CdTe grain after the annealing process will be introduced, and the effect of various conditions for electro-deposition process will be discussed.
1. Experiments

1.1 Cd or Te Electro-Deposition

The total system of experimental apparatus is shown in Fig. 1. A cathodic thin plate sized 10mm x 10mm square was inserted in ammonia alkali electrolyte. The pH of electrolyte was kept to be constant (11–12) due to ammonia sulphate buffer solution. The electrolyte cell was set in the bore of a superconducting magnet. The position of the cathode was adjusted to be the region of maximum value of the magnetic field, where the direction was vertical as shown in Fig. 1. A water circulating system with a water pump and a heating bath controlled the temperature of the whole cell. The electrical potential was also controlled to constant value by means of an Ag/AgCl standard electrode and a potentiostat.

Using this apparatus, Cd thin film was deposited from CdSO$_4$ solution, and Te thin film was deposited from TeO$_2$ solution with ammonia buffer solution under intense magnetic field up to 5T. The cathodic plate was set in the cell in two ways, one was parallel to the magnetic field and the other was perpendicular to that. Experimental conditions are listed Tab.1.

![Fig.1. Total system of electro-deposition process and the position of cathodic plate.](image)

### Table 1. Experimental conditions.

<table>
<thead>
<tr>
<th>Electrodeposition method</th>
<th>Cd</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference electrode</td>
<td>Ag/AgCl electrode (0.197V vs. SHE)</td>
<td></td>
</tr>
<tr>
<td>Cathode potential (vs SHE) / V</td>
<td>-1.00</td>
<td>-1.00</td>
</tr>
<tr>
<td>Bath composition / mol/l</td>
<td>CdSO$_4$ (\cdots) 0.1</td>
<td>TeO$_2$ (\cdots) 0.1</td>
</tr>
<tr>
<td>Imposed magnetic field / T</td>
<td>0, 5</td>
<td>0, 5</td>
</tr>
<tr>
<td>Temperature / K</td>
<td></td>
<td>343</td>
</tr>
</tbody>
</table>

1.2 CdTe Electro-Deposition

After the electro-deposition of Cd or Te layer, CdTe film was deposited epitaxially. The experimental conditions were same as that in Tab.1. However, the electrolyte was ammonia alkali buffer solution including both Cd ions and Te ions. And cathode potential was -0.75V vs. SHE. CdTe crystal has a cubic structure, so that crystal orientation cannot be expected. But the texture of crystals can be aligned by epitaxial growth.
1.3 Heat Treatment

Generally, crystal grains with same texture have the potential to become a large crystal during heat treatment, because the interfacial energy of the boundaries between the same textured grains is considered to be small. Actually, the annealing temperature was set from 573K to 673K. And the annealing time was set up to 60 min.

2. Results and discussion

In the electro-deposition process of the basic layer, crystal orientation due to anisotropy in magnetic susceptibility can be obtained. In hexagonal crystals, generally, the magnetic susceptibility along c-axis is different from that along a,b axis. In crystallization process under magnetic field, crystals can align toward the specific direction where the magnetization energy becomes minimum.

\[
U = -\frac{\chi}{2\mu_0(1 + N_\chi)} B^2
\]  

(2.1)

Magnetization energy, U, defined by Eq.(2.1) is proportional to square of magnetic field, B, and the coefficient includes the magnetic susceptibility, \(\chi\).

Fig.2 shows the deposited Cd surface under 5T imposition. In the case of Cd, \(\chi_c\) is smaller than \(\chi_{a,b}\), so that the Cd crystals of flake shape are highly aligned as the c-axis of the crystal is coincide with the direction of magnetic field. In the case of Te deposition, crystal orientation appears in the same way.

![Fig.2. Typical surface morphology of electro-deposited Cd.](a) B is parallel to cathode. 10µm (b) B is perpendicular to cathode. 10µm

In XRD pattern analysis of the Cd deposited surface, the consistent results with the photograph are obtained. In the case that magnetic field is perpendicular to the cathode, intensity of (002) plane (c-plane) of Cd increases as increase of magnetic field. On the other hand, intensity of (100) plane (a,b-plane) decreases as increase of magnetic field. The same tendency is found out for Te deposition.

It is expected that epitaxial deposition of CdTe grains will form large grains in annealing process. Fig.3 shows the effect of annealing temperature on the grain size of CdTe, which is derived from scherrer’s equation according to XRD peak pattern. The grain size becomes large as increase of the annealing temperature. And combined electro-deposition process is advantageous for the grain growth even if the magnetic field does not applied, as shown in Fig.3. It is considered that the Cd or Te grain has preferable orientation originally.
Fig. 3. Relation between annealing temperature and the size of deposited CdTe grains without magnetic field.

Fig. 4 shows the comparison between the grain size with and without magnetic field imposition after the annealing process in the case of Te-CdTe combined deposition. At 400°C, the grain size of epitaxial deposited CdTe is about 1.5 times as large as that of normal deposited CdTe. The same result is obtained for Cd-CdTe combined deposition. And the maximum value of the grain size is obtained in the case of Te-CdTe combined deposition and annealing process.

Fig. 4. Comparison of the grain size of electro-deposited CdTe after the annealing process.

Conclusions

In order to manufacture CdTe semi-conducting film with large crystals, a new method are proposed, where CdTe crystals are electrically deposited onto highly oriented crystals of Cd or Te film and then annealed. Obtained results are listed as follows.

1. Cd or Te base layer can be oriented strongly by the imposition of intense magnetic field, because the hexagonal structure has anisotropy for the magnetic susceptibility.
2. Two steps of electro-deposition process and successive annealing process can produce large grains.

References

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