EFFECT OF COMPLEXING AGENT ON SPRAY DEPOSITED CdTe THIN FILMS

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ABSTRACT

Te rich CdTe thin films have been prepared by spray pyrolysis technique using a complexing agent Ethylene-Diamine-Tetra-Acetic acid (EDTA) in the precursor solution. The films are characterized using XRD, XPS and PL techniques. XRD studies indicates that the films consist of a mixture of CdTe and Te and the Te peak intensity varies with EDTA concentration. XPS study iners that there is a change over in chemical environment of Te. A broad photoluminescence peak at 1.40 eV is observed in the films with no complexing agent, which can be resolved into two peaks 1.43 and 1.40 eV. The intensities of both peaks increase with EDTA concentration. XPS studies indicates that there is a change over in chemical environment of Te. Therefore, the best strategy will be to introduce a thin Te rich CdTe layer as part of the absorber layer deposition process. Since the complexing agents form stable complexes with metal cations, this can be a convenient method for preparation of CdTe thin films, which provide controlled stoichiometry and will be particularly useful for preparing Te rich films on the surface of p-CdTe. In the present study we have used Ethylene-diamine-tetra-acetic acid (EDTA) as a complexing agent in the precursor solution and have demonstrated the preparation of CdTeTe films with varying Te composition using spray pyrolysis technique.

2. EXPERIMENTAL DETAILS

The spray solution is prepared from a mixture of water, ammonium hydroxide, hydrazine hydride and hydrochloric acid. Cadmium and tellurium are added in the form of cadmium chloride (CdCl₂) and tellurium oxide (TeO₂) with concentration of ~ 0.02 M. Hydrazine hydride is used as a reducing agent to obtain Te⁴⁺ ions from the Te⁶⁺ ions [17]. Ethylene Diamine Tetra Acidic Acid (EDTA) is added as a complexing agent for the spray solution with the concentration of 0.02M and 0.05M. Solution pH value is adjusted to 11.2 by the addition of hydrochloric acid. Flow rate of the solution is ~ 1-1.5 ml/min for the deposition on glass substrates kept at 400 °C during spray.

One of the key issues in manufacturing CdTe/CdS thin film solar cell is the formation of ohmic and stable back contact. It is very difficult to prepare a highly doped p-CdTe thin film for low resistance contact because of its self-compensation effect [10-11]. The back contact commonly consists of a few nm thick elemental Te layer formed by etching with NP-etch or Br-methanol etch to create a p⁺ layer for pseudo-ohmic contact. The adverse effects of chemical etching process are formation of metastable Te-rich CdTe surface and widening of the grain boundaries which leads to the diffusion of back contact metal easily via V_cor states and along Te-rich grain boundaries [15].
homogeneous distribution of grains than the films deposited without complexing agent. With increasing EDTA concentration the grain size is reduced. It infers that the surface morphology is dependent on EDTA concentration. Similar type of granular structure was also observed for the Te rich CdTe films by electroplating after using ethylenediamine as a complexing agent in the electrochemical bath [3].

X-ray diffraction studies are carried out to determine structure and the phases in the films. Films are polycrystalline with random orientation and show no sign of texturing. Fig. 2 shows the XRD patterns of the samples A, B and C. Sample A shows CdTe sharp peaks from (111), (220) and (311) planes of the cubic phase, the peak positions are in good agreement with the standard ASTM X-ray Powder file data (15-770) for cubic CdTe. Along with CdTe the satellite CdTeO$_3$ peaks are also observed. On the other hand films deposited with complexing agent EDTA show additional peaks of Te also. The Te peak intensity increases with EDTA concentration, whereas the peak intensity of CdTe phase is decreased. The additional tellurium peaks are from (100), (101) and (102) planes of the hexagonal phase for sample C. Peak positions are agreement with standard ASTM X-ray Powder file data (4-554) for hexagonal Te.

EDTA reacts with Cd ions to form very stable complexes. It is a less volatile hexadentate chelating agent that reacts with metal cations to form very stable complexes [18]. Then the cations (Cd$^{+2}$) are released at a slower rate during the pyrolytic reaction on the hot substrate that leaves the anions (Te$^-$) free leading to the formation of Te rich CdTe film. One can see clearly in Fig 2(b), when the same amount of EDTA (0.02 M) present in the CdTe (0.02 M) precursor solution, it is promoting the CdTe in (111) oriented growth and having nearly equal intense Te (101) peak. Thus the molar ratio of EDTA to the total metal cation is very important for controlling the stoichiometry of the compound semiconducting films. Similar observations were made for electroplated CdTe thin films after using the ethylenediamine as a complexing agent [3]. Similar peaks of Te are also observed in case of non-stoichiometric CdTe films deposited with physical vapor deposition [19].

For understanding the Te chemical environment X-ray photoelectron spectroscopy study on Te 3d core levels is carried out. The XPS spectra in Fig. 3 clearly show the shift in Te binding energy of 3d$_{5/2}$ core electron from 573.0 to 576.5 eV [20] after using the complexing
agent. In sample A, Te is existing mainly in Te$^{3+}$ state from Te-Cd bond, along with a satellite peak of Te$^{4+}$ state due to surface oxidation of Te. In sample B, Te 3d$_3/2$ state split into two peaks with nearly equal intensity means Te exists in both the states, since Cd availability is partially reduced and Te is equally distributed (Te-Cd and Te-O). The complete change over in chemical environment is observed in case of sample C, where peak corresponding to the Te-O environment increases at the expense of the Cd-Te peak confirming the role of EDTA in restricting the release of Cd for CdTe formation and leaving Te in elemental form.

Photoluminescence spectra of the CdTe film deposited without complexing agent and film deposited with EDTA $= 0.05$ M are shown in Fig. 3. The luminescence near band edge and due to the exciton in CdTe film is absent. It could be due to the polycrystalline nature, the grain boundaries generally provide an effective route for nonradiative process. The broad luminescence band near 1.4 eV in Fig. 3(a) of sample A shows that the luminescence process is non elemental. After deconvolution we can resolve it into two peaks at 1.43 eV and 1.40 eV. In case of sample C as shown in Fig. 3(b) the Photoluminescence intensity of both the peaks is enhanced, and satellite peaks at 1.49 and 1.33 eV are also observed.

4. CONCLUSIONS

In conclusion, the role of complexing agent (EDTA) to modify the properties of CdTe thin film prepared by spray pyrolysis has been studied. The concentration of complexing agent in spray solution can be optimized to obtain Te rich CdTe films by keeping the constant Cd(II)/Te(IV) concentration ratio and pH values. The variation in Te concentration can be useful in preparing Te rich surface as a part of deposition process, which can make the contact formation a very easy process for CdTe/CdS thin film solar cells.

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REFERENCES


