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ABSTRACT

We report on the growth, grain enhancement, doping, and electron mobility of cadmium selenide (CdSe) thin films deposited using the thermal evaporation method. The optical measurement shows CdSe is a direct bandgap material with an optical bandgap (E_{gap}) of 1.72 eV. CdSe thin films were deposited on fluorine doped tin oxide glass substrates with different thicknesses, and grain size and mobility were measured on the films. CdCl₂ was deposited on the films, and the films were subjected to high temperature treatment for several hours. It was found that both grain sizes increased significantly after CdCl₂ treatment. The mobility of electrons was measured using the space charge limited current technique, and it was found that the mobility increased significantly after CdCl₂ treatment. It was discovered that postdeposition selenization further improved the electrical properties of CdSe thin films by increasing the electron mobility-lifetime product and the photo/dark conductivity ratio. CdSe films after postselenization also showed significantly lower values for midgap states and Urbach energies for valence band tail states.

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I. INTRODUCTION

CdSe is a II-VI group semiconductor chalcogenide which is potentially an attractive material for photovoltaic energy conversion since its bandgap is around the value (∼1.7 eV) needed for use in a tandem junction solar cell with silicon acting as the bottom cell.1–3 Theoretical calculations indicate that it is possible to attain a thermodynamic efficiency of ∼45% in a tandem cell of CdSe and c-Si.4 CdSe is a binary compound; hence, it is easier to achieve stoichiometry than in a ternary or quaternary material. CdSe is not water soluble and does not thermally decompose, unlike Pb-halide perovskites.5 It is a direct bandgap semiconductor,6 and, consequently, only a thin film is needed to absorb photons. CdSe thin films can be deposited using different techniques including thermal evaporation,7 close-spaced sublimation,8 and sputtering.9 In this work, we report on deposition of CdSe thin films using physical vapor deposition at a high growth temperature of ∼400°C with different thicknesses in the range of 0.5 μm–3 μm. We show that postdeposition treatments using CdCl₂ increase the grain size and mobility of CdSe significantly. Further high temperature selenization treatment under a Se flux serves to further increase the mobility.

II. EXPERIMENTAL PROCEDURE

For optical characterization, a glass/CdSe structure was prepared using thermal evaporation at a working pressure of 3 × 10⁻⁶ Torr. Luxel Radak furnaces with excellent temperature control were...
used to deposit the films. Two Radak furnaces could be used to deposit CdSe and Se simultaneously. Typical film thicknesses were in the range of 0.5–3 μm. For morphological and electrical characterization, films were deposited on various substrates, including glass, fluorinated tin oxide (FTO), and FTO coated with n-CdS and Si wafers. Next, CdCl₂ treatment was carried out on some of the samples. The CdCl₂ treatment consisted of spin coating of a 2 wt. % solution of CdCl₂ in deionized (DI) water (2 g/100 ml) followed by thermal annealing under a nitrogen atmosphere at 450 °C for 30 min inside a quartz tube. For the photoconductivity experiment, after CdSe evaporation, the postselenization step was performed at 450 °C on three samples for 30 min, 60 min, and 120 min under a nitrogen flow inside the quartz tube. The optical properties were measured using a Cary 5000 UV-Vis-NIR spectrophotometer in a 400–2500 nm wavelength range.

III. RESULTS AND DISCUSSION

A. Optical properties

Optical absorption data, the absorption coefficient $\alpha$ vs E, where E is the photon energy, of the 1 μm CdSe film deposited at 400 °C on a glass substrate is shown in Fig. 1(a). The plot of $(\alpha \cdot E)^2$ vs E is shown in Fig. 1(b). It shows linear dependence with an intercept at 1.72 eV, implying a bandgap of 1.72 eV.

B. Surface morphological analysis under grain enhancement

The surface morphology of the various CdSe films was assessed using a SEM. The data are shown in Fig. 2. The increase in the grain size as the thickness increases is to be noted.
After deposition, a heat treatment when coated with CdCl$_2$ was found to have a significant impact on the grain size, achieving grain enhancement, as shown in Fig. 3. The grain sizes after grain enhancement are about 1 $\mu$m, 1.3 $\mu$m, 1.5 $\mu$m, and 1.9 $\mu$m for the films whose thicknesses were 0.5 $\mu$m, 1 $\mu$m, 2 $\mu$m, and 3 $\mu$m, respectively. SEM images clearly show that the surface of the film becomes flat and smooth after the CdCl$_2$ treatment.

In Fig. 4, we show the cross-sectional SEM image of one of the grain enhanced films, showing that the grain enhancement is through the entire film.

C. Electrical properties under grain enhancement

The electron mobility of CdSe films in the direction of growth was measured using the space charge limited current (SCLC) technique. In this method, one uses a sample with ohmic contacts on both sides and measures the current vs voltage characteristic. When the injected charge density exceeds the thermal charge density, the current follows a $J \propto V^2$ relationship. The mobility can be calculated from the slope using the following equation:

$$J = \frac{9}{8} \epsilon \mu \frac{V^2}{L^3},$$

where $J$ is the current density, $V$ is the voltage, $L$ is the sample length, $\epsilon = \epsilon_0 \epsilon_r$, where $\epsilon_0$ is the absolute permittivity and $\epsilon_r$ is the relative permittivity of the material, and $\mu$ is the mobility of the carrier. Since CdSe is generally n-type, we used the FTO/n$^+$-CdS/CdSe/PCBM/Al structure, where n$^+$-CdS and PCBM play roles as ohmic contacts on both sides for the n$^+$-n-n$^+$ structure, as shown in Fig. 5.

Carrier concentration also can be measured using the following equation:

$$n = \frac{1}{q} \frac{V_{SCLC}}{L^2},$$

where $n$, $q$, and $V_{SCLC}$ are the carrier concentration, electron charge, and voltage at the intersection of the space charge limited current region and ohmic region, respectively.

Figure 6 shows current density vs voltage and voltage square for the as-deposited and grain-enhanced CdSe films with thicknesses of 0.5 $\mu$m, 1 $\mu$m, 2 $\mu$m, and 3 $\mu$m. The figures show a distinct $I \propto V^2$ behavior at higher voltages. The slope of this line yields a value for mobility. Note that the increase in the grain size with thickness, as shown in Fig. 2, precludes verifying the scaling factor of length $L$. 
in Eq. (1). Because of this behavior of the increase in the grain size with thickness, and hence the increase in mobility with thickness, it is likely that the real mobility at higher grain sizes is actually larger than that shown in Fig. 7.

In Fig. 7, we show the mobility vs thickness for as-deposited and after grain enhancement of CdSe thin films. Grain enhancement clearly leads to higher mobilities. The highest mobility that we have achieved is about 3.5 cm²/V s for large grain CdSe films in the range of 2 μm.

D. Influence of post-grain-growth selenization on photo and dark conductivity

Since the grain growth is done at relatively high temperatures, there is a potential loss of Se during such a procedure. To see if this is the case, one can measure dark conductivity and photoconductivity of the films and also study the tail state density both after grain growth and after growth followed by selenization.

Photoconductivity was measured on as-deposited and post-selenized CdSe thin films. The results for the photoconductivity and light-to-dark conductivity ratio are shown in Fig. 8. It clearly shows that both photoconductivity and light-to-dark conductivity increases as a function of selenization time. From the photoconductivity, one can deduce the electron mobility-lifetime (μτ) product.
A large mobility-lifetime product indicates that the electron recombination center density has decreased. The mobility-lifetime product can be deduced from photoconductivity by knowing the photon generation rate $G/cm^3$, given by

$$G = \frac{N_{abs}}{t}, \quad (3)$$

where $N_{abs}$ is the amount of absorbed photon flux, and $t$ is the thickness of the film. The amount of absorbed photon flux is given by

$$N_{abs} = N_0 (1 - R) (1 - \exp(-a t)), \quad (4)$$

where $N_0$, $R$, $a$, and $t$ are the incident photon flux, reflection, absorption coefficient, and thickness, respectively. Finally, the photoconductivity and mobility-lifetime product can be expressed by the following equations:

$$\Delta \sigma = \sigma_{\text{light}} - \sigma_{\text{Dark}}, \quad (5)$$

$$\mu \tau = \frac{\Delta \sigma}{q G}, \quad (6)$$

where $\sigma_{\text{light}}$, $\sigma_{\text{Dark}}$, and $\Delta \sigma$ are the light conductivity, dark conductivity, and photoconductivity, respectively.

The mobility-lifetime product vs time of post-deposition selenization curve is shown in Fig. 9. The figure shows that the $\mu \tau$ product increases by about 5 times after 120 min of selenization.

### E. Measurement of tail state density

All polycrystalline materials have tail states near the conduction and valence bands because of the disorder in the crystalline network. For tail states near the valence band, which are filled with electrons since the material is n-type, an accurate way of measuring them is to use sub-bandgap photoconductivity vs photon energy. The sub-bandgap photons excite electrons from the tail states into the conduction band, and assuming that the matrix elements coupling these states to the conduction band are independent of energy, a plot of subgap photoconductivity vs photon energy yields the density of tail states vs energy. This method has been widely used to deduce tail state and midgap state densities in a-Si:H and perovskites.

In Fig. 10, we show the deduced density of tail states as a function of photon energy ($E$) for three films, without grain enhancement, with grain enhancement, and with post-selenization. The Urbach energy of tail states, $E_u$, can be deduced from the following equation:

$$a = a_0 \exp \left( - \frac{E - E_v}{E_u} \right), \quad (7)$$

where $E_v$ is energy of the valence band. The Urbach energy for valence band tails is also reduced with selenization and has a value of 21 meV for the best film. This value is in the same range for other efficient photovoltaic materials such as perovskites. The figure also shows that at lower energies, there is flattening of the curve, indicating the presence of midgap states and that selenization has also reduced the density of such states. This, of course, is the reason why the electron $\mu \tau$ product increased after selenization.

### IV. CONCLUSIONS

CdSe thin films were prepared on glass and FTO/CdS substrates by the thermal evaporation method at 400 °C with different thicknesses. CdCl$_2$ heat treatment was carried out at 450 °C for different times inside a quartz tube in a nitrogen atmosphere. It is seen that high temperature heat treatment with CdCl$_2$ yields significant grain enhancement. Selenization after grain-enhancement was shown to improve the photoconductivity and the photo-to-dark conductivity ratio. The mobility-lifetime product for electrons was measured and
was found to increase with selenization time and be in the range of $5 \times 10^{-6}$ cm$^2$/V. Tail state densities and the Urbach energy of the tail states near the valence band were measured, and it was found that selenization reduced the tail state densities and also reduced the midgap densities. The films had a low Urbach energy of 21 meV after selenization.

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