EARTH ABUNDANT MATERIALS FOR HIGH EFFICIENCY HETEROJUNCTION THIN FILM SOLAR CELLS

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ABSTRACT

We investigate earth abundant materials for thin-film solar cells that can meet tens of terawatts level deployment potential. Candidate materials are identified by combinatorial search, large-scale electronic structure calculations, and literature reviews. We identified cuprous oxide (Cu_2O) as a prototype candidate for investigation as an absorber layer in thin film solar cells. Cu_2O thin films are deposited by reactive DC magnetron sputtering and characterized. In order to tailor electrical properties, we modify grain structure, and add defects that enhance electron transport, maintaining desired optical gap.

INTRODUCTION

Photovoltaics (PV) is perhaps the most promising renewable energy source that can meet the global energy demand while keeping low concentrations of CO_2 in the atmosphere. To become a major energy source, module costs should be reduced significantly and energy conversion efficiencies should be increased. In terms of reducing module cost, thin film solar cells are a viable option due to their lower material usage and inexpensive manufacturing potential. However, current materials for thin film solar cells such as CdTe and CIGS suffer from concerns over resource scarcity (e.g., Tellurium and Indium)[1] and toxicity (e.g., Cadmium) respectively and are therefore limited to sub-terawatts deployment. We are developing thin film solar cells with the inherent advantages of thin film materials, and can be deposited atop Si substrates. The material should have proper optical and electrical properties including a direct bandgap (1.6-2.0 eV).

COMPUTATIONAL BANDGAP-PREDICTION

In order to find good candidate materials efficiently, we have developed computational methods that predict the bandgap of a given material. The prediction of bandgap can be carried out to various levels of accuracy by using different computational methods, with more computationally intensive methods generally producing more accurate results.

The most efficient method is the calculation of the bandgap using standard Density Functional Theory (DFT). Although DFT typically underestimates the bandgap compared to experimental values, it is still useful as a first screening tool. We found by investigating hundreds of compounds that the most efficient way to obtain the points in reciprocal space (k-points) corresponding to the valence and conduction band edges depends on the crystal symmetry of the compound. By automating the selection of k-points based on the crystal symmetry, we have reduced the computational effort to obtain a DFT estimate of the bandgap by an average of 70%.
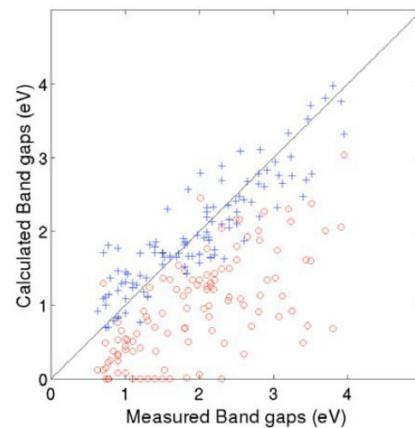

Fig. 1. Improvement in band gap prediction accuracy. Calculated band gaps are plotted against the experimentally measured values for 111 compounds. Red circles are obtained from standard DFT (mean error 1.0 eV) and blue crosses are from newly-developed method taking into account the dielectric screening (mean error 0.3 eV).

To improve on the accuracy of bandgap prediction, existing methods typically require 100-1000 times the computational effort of DFT. We have developed improvements in prediction accuracy of the DFT bandgap, without significant increase in computational efforts, by making use of the dielectric screening properties of the material. As a result, we have made improvements in the mean error of the estimated bandgaps from 1.0 eV to 0.3 eV for compounds in the relevant bandgap range, as shown in Fig. 1. When combined, the new efficiency and accuracy allow for more rapid and reliable screening of the thousands of compounds for suitability as PV materials.

Compound	Formula	Bandgap
Aluminum Dodecarboride	AlB_{12}	1.9 eV
Calcium Silicide	Ca_2Si	1.9 eV
Cuprous Oxide	Cu_2O	1.9-2.0 eV
Copper Nitride	Cu_3N	1.2-1.9 eV
Silicon Diphosphide	SiP_2	1.9 eV
Zinc Diphosphide	ZnP_2	1.7-2.2 eV
Zinc Phosphide	Zn_3P_2	1.4-2.2 eV
Zirconium Sulfide	ZrS_2	1.7 eV

Table 1. Candidate semiconductor compounds

MATERIAL SELECTION

Over 500 semiconductor compounds were found from combinatorial materials search. We have analyzed material's availability based on the abundance in Earth's crust and manufacturing production capacity. We derived a list of low-cost elements that can meet terawatts level deployment. Computational prediction of bandgap and literature reviews were performed which reduced the list to tens of earth-abundant semiconductor compounds (Table 1). As the first selection for thin film solar cells materials, cuprous oxide (Cu_2O) was investigated.

THIN FILM DEPOSITION

Experimental

Cu_2O films were deposited by DC magnetron sputtering using AJA international ATC 2200. The base pressure of the chamber was 5.6×10^{-5} Pa. A constant power (50-250W) sputtering mode was used with 99.999% pure Copper target. Ar, O_2 and N_2 gas flows were controlled from 0 to 40 sccm for reactive sputtering
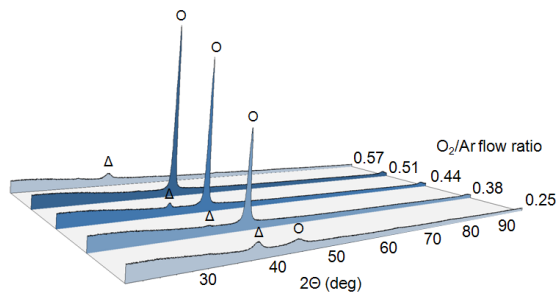
deposition. Quartz lamps were used to control substrate temperature from room temperature up to 850°C during film deposition as well as post-annealing processes. 2mm-thick soda lime glass and quartz substrates are cleaned in acetone for 5 minutes and rinsed by DI water before deposition.

Film thickness was measured by a Dektak surface profilometer, and resistivity was measured by a 4-point probe station. The phase and crystal structure of Cu_2O was studied using PANalytical's X'Pert PRO materials research diffractometer with Cu-Kα radiation. Optical absorption and reflection properties were measured by Cary 500i UV-Vis-NIR dual-beam spectrophotometer. A JEOL 6320FV field-emission high-resolution SEM was used to characterize the morphology of Cu_2O thin films.

Result

Copper has two stable oxide phases: CuO and Cu_2O. In order to control the phase, sputtered copper flux and oxygen partial pressure were varied by changing the sputtering power and the argon / oxygen flow rate ratio. From the X-ray diffraction pattern in Fig. 2, optimal sputtering parameters were determined to obtain a highly-crystalline Cu_2O film with a dominant grain orientation of (111). The optical bandgap was

Fig. 2. XRD patterns of as-deposited films at room temperature with different O₂/Ar flow rates (Δ:Cu₂O (200), O:Cu₂O(111))
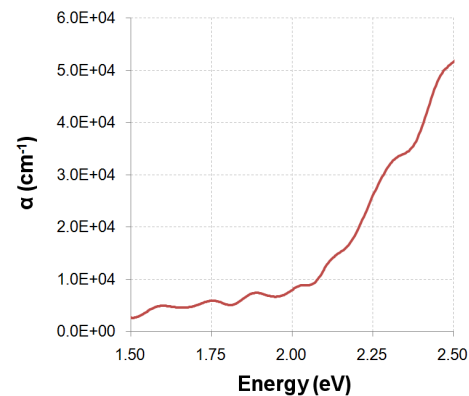

Fig 3. Experimental light absorption coefficient of as-deposited Cu_2O thin film at room temperature

determined to be ~2.0 eV, as shown in Fig. 3. The resistivity varied between 1.7×10^3 and 4.3×10^5 Ω-cm.

In order to use Cu_2O thin films as a solar cell absorber layer, the columnar grain structure with a large grain size is preferred [3] to minimize carrier interactions with grain boundaries and thus improve carrier mobility. We increased the substrate temperature during film deposition and annealed Cu_2O films in a vacuum chamber for morphology modification. Increasing the substrate temperature during deposition resulted in larger grains. In Fig. 4, Cu_2O films deposited at 850°C (a) showed a columnar grain structure with 348nm average grain size, while films deposited at room temperature (b) have 54nm average grain size.

It was found that undoped Cu_2O films have p-type conductivity due to Cu vacancy with acceptor level 0.25-0.4 eV.[4,5] Nitrogen is reported to act as a p-type dopant with a shallow state at VB+0.14 eV.[5] During the deposition process, nitrogen gas was introduced at room temperature. The resistivity of the Cu_2O film decreased to 5.5×10^2 Ω-cm as the N_2 flow rate increased to 1.0 sccm (Fig. 5).

CONCLUSIONS

In this collaborative effort, we have developed computational tools that enable predictive screening for compounds with desired optoelectronic properties. The enhanced accuracy of bandgap prediction enables the identification of appropriate PV materials made from Earth-abundant elements. We have determined the elemental basis set comprising Earth-abundant materials, both from the perspective of resource availability as well as annual production. We reviewed the experimentally determined physical properties of hundreds of Earth-abundant semiconductor compounds, and selected ten of the most promising candidates for further exploration. Of these, we deposited Cu_2O thin films as one of the more promising candidate compounds, and tailored its structural properties, a precondition towards enabling high-efficiency photovoltaic devices.
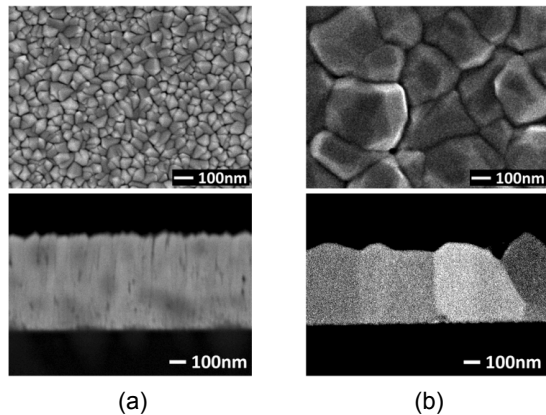
Fig. 4. Top and cross-cut SEM images of Cu_2O thin films deposited at (a)room temperature, and (b)850°C
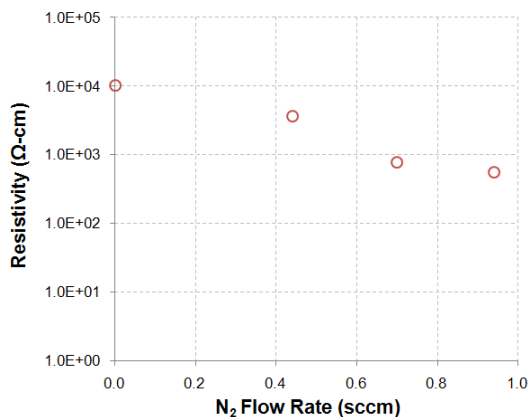
Fig. 5. Resistivity changes by introducing nitrogen gas during deposition

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