CIS Nanocrystals with Inorganic Ligands for Photovoltaics Devices

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Abstract:

Films of copper indium diselenide ($CuInSe_2$ or CIS) nanocrystals capped with inorganic ligands were studied for use in photovoltaic devices (PVs). CIS nanocrystals were synthesized by colloidal arrested precipitation with oleylamine capping ligands. Oleylamine was exchanged for inorganic metal chalcogenide complex (MCC) ligands. These nanocrystals were dispersed in dimethyl sulfoxide, enabling the formulation of a "solar ink" that was spray-coated onto molybdenum (Mo)-coated glass substrates. The nanocrystal films were thermally annealed under argon and limited sintering was observed. Typically, grain growth of CIS films requires high temperature (> 500°C) and Se-rich atmosphere.

Introduction:

As energy demand continues to increase, technologies that can harness and convert sunlight to electricity efficiently and economically are becoming more and more needed. Photovoltaic (PV) devices convert light directly into electricity. Silicon solar cells currently dominate the PV market, but silicon-based PVs are still too expensive. New PV technology is needed to make PV solar energy cost-competitive with fossil fuels. Copper indium selenide (CIS) is one promising thin film semiconductor material for lower-cost PVs. One approach to CIS deposition with potentially very low cost is to generate solar inks of nanocrystals that can be deposited from solution under ambient conditions. Using this approach, CIS nanocrystal-based PVs have achieved power conversion efficiencies up to 3% without high temperature processing of the absorber layer [1, 2].

The relatively low device efficiencies have been due to organic ligands on the nanocrytsals, which prevent agglomeration and allows solution processing but create an electrically insulating barrier between nanocrystals. Organic ligands can be replaced with inorganic metal chalcogenide complexes (MCCs) to improve electrical conductivity of nanocrystal films. Recently, PV devices have been made with inorganic ligand-capped nanocrystals, but with low efficiency [3].

One additional limitation was the need to process with hydrazine, which is environmentally unfriendly. We have been able to develop inorganic ligand-capped CIS nanocrystals that disperse in dimethyl sulfoxide (DMSO), a polar organic solvent that is environmentally friendly and easier to handle than hydrazine, in the nanocrystal film processing and have used MCC ligands to cause grain growth in CIS nanocrystals without selenization.

We also examined the films after a high temperature heat treatment. One approach to obtaining higher efficiencies from nanocrystal absorber layers is to sinter them into crystalline films. Usually sintering requires Se vapor in addition to high temperature. Annealing the nanocrystal films at high temperature under Ar did lead to a small amount of crystal grain growth, presumably enabled by the inorganic Se-containing capping ligands.

Methodology:

Colloidal oleylamine-capped CIS nanocrystals were synthesized by arrested precipitation as previously described [3, 4]. Ligand exchange was performed in a nitrogen-filled glove box by adding the nanocrystals to 0.5 ml of 0.25 M In_2Se_4-MCC ligand, and 3 ml of hydrazine. After stirring for two days, the nanocrystals were transferred from the toluene to the hydrazine phase and the toluene was decanted. The nanocrystals were precipitated by adding 8 ml acetonitrile, followed by centrifugation. The particles were redispersed in 1.5 ml of dimethyl sulfoxide (DMSO).

CIS nanocrystals dispersed in DMSO were spray-cast onto Mo-coated glass substrates heated to 150°C. The nanocrystal films were annealed in an argon atmosphere at 500°C-600°C for 20 minutes. PV devices were then fabricated and tested as described in the literature [2]. Nanocrystal films were also characterized by scanning electron microscopy (SEM) and x-ray diffraction (XRD).

Results and Discussion:

CIS Nanocrystals Before Sintering. Figures 1 and 2 show transmission electron microscopy (TEM) images of oleylamine-capped CIS nanocrystals before and after exchanging with inorganic ligands. The nanocrystals are approximately 15 nm in diameter and do not change size after ligand exchange, but do appear to be slightly more prone to aggregation.

CIS nanocrystal films were deposited onto Mo-coated glass substrates and were annealed under Ar at temperatures between 500°C-600°C. Figure 3 shows an SEM image of the annealed nanocrystal film at 575°C and Figure 4 shows XRD data for nanocrystal films annealed at various temperatures. There was a small, yet noticeable, amount of sintering and crystal grain growth. The <112> peak in the XRD patterns in Figure 4 became slightly sharper as well after annealing, consistent with grain growth. PV devices fabricated from these films showed only a small PV response with a very low device efficiency of only 0.2%. More device tests are required to determine whether these materials will be suitable for PVs.

Conclusions:

CIS nanocrystal films capped with inorganic In_2Se_4-MCC ligands and dispersed in DMSO, which is not toxic like hydrazine, can be deposited safely under ambient conditions. These inorganic-capped CIS nanocrystals appear to exhibit sintering and crystal grain growth with high temperature annealing without Se vapor. The preliminary device tests using these nanocrystal films gave low efficiencies, but the materials require further study.

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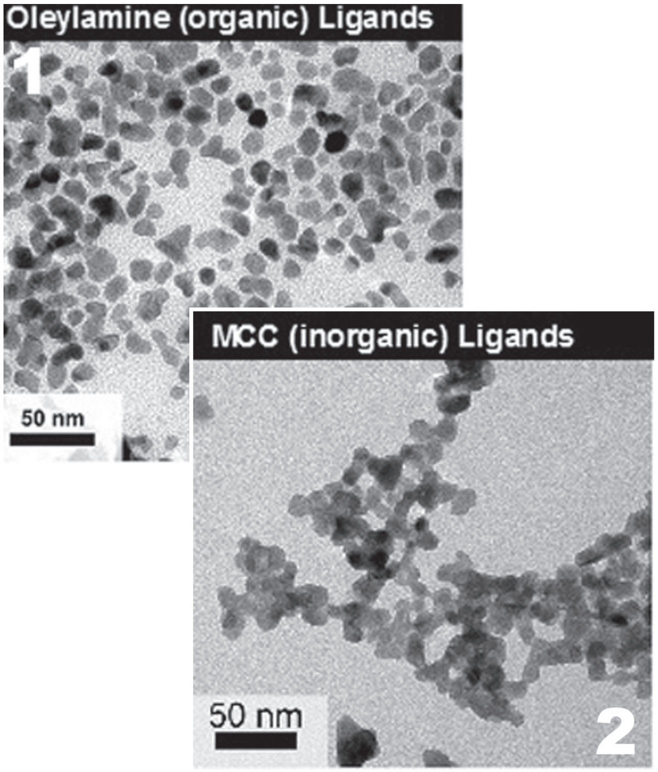
References:

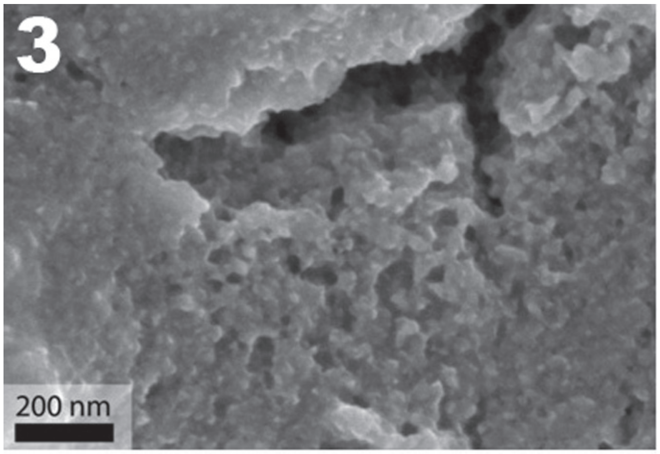
[1] Panthani, M. G.; Akhavan, V.; Goodfellow, B.; Schmidtke, J. P.; Dunn, L.; Dodabalapur, A.; Barbara, P. F.; Korgel, B. A. J. Am. Chem. Soc. 2008, 130, 16770-16777.

[2] Akhavan, V. A.; Goodfellow, B. W.; Panthani, M. G.; Reid, D. K.; Hellebusch, D. J.; Adachi, T.; Korgel, B. A. Energy Environ. Sci. 2010, 3, 1600-1606.

[3] Stolle, J. C.; Panthani, M G.; Harvey, T. B.; Akhavan, V. A.; Korgel, B. A. ACS Appl. Mater. Interfaces, 2012, 4, 2757-2761.

[4] Jiang, Chengyang; Lee, Jong-Soo; Talapin, Dmitri V. J. Am. Chem. Soc. 2012, 134, 5010-5013.





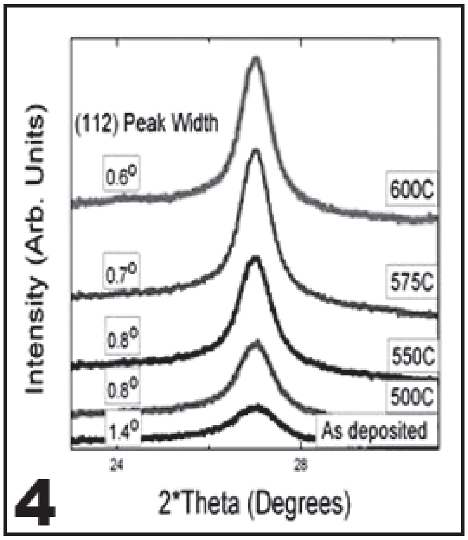


Figure 1, top left: A TEM of oleylamine-capped CIS NCs.

Figure 2, top right: After exchange, aggregated MCC-capped CIS NCs.

Figure 3, middle: SEM of MCC-capped CIS NCs annealed at 575°C.

Figure 4, bottom: FWHM of the 112 peak of MCC-capped CIS NCs annealed from 500°C-600°C.