



## Plasmonic modification of CdTe thin films by gold nanoparticles: Methods, difficulties and solutions



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### ABSTRACT

Despite numerous theoretical studies on CdTe absorbers with embedded metal nanoparticles (NPs), no technological reports are found. We present an experimental study of 300-nm-thick CdTe absorber layers deposited by close spaced sublimation with incorporated gold NPs to obtain the effect of surface plasmon resonance (SPR). Gold NPs were formed from a  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  solution in ethanol and deposited by spin coating or spray pyrolysis on the top of CdTe film. As alternative, sputtering followed by air annealing of gold thin layer was applied to form Au NPs between the glass substrate and the CdTe layer. The properties of these structures were studied by UV–VIS spectroscopy, scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction.

The SPR effect was observed in the wavelength region of 570–590 nm for CdTe layers, with Au NPs measuring 30–40 nm in size. At the increased amount of sprayed  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  solution the nanoparticles were agglomerated into grains and the SPR peak shifted to longer wavelengths. In the case of spin coating the  $\text{HAuCl}_4$  solution decomposes on the CdTe surface and by chemical reaction contributed to the substantial removal of the CdTe. Sputtering and spray pyrolysis methods did not change the bulk CdTe layer and introduced the plasmonically enhanced absorption, but led to the formation of additional inter-metallic phases, such as AuCd,  $\text{Au}_{0.3}\text{Te}_{0.7}$  or  $\text{AuTe}_2$ . The  $\text{Au}_{0.3}\text{Te}_{0.7}$  phase is supposed to play the role of a shell for Au NPs shifting the 592 nm SPR peak to lower wavelengths. Chemical processes responsible for these effects are discussed.

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### 1. Introduction

In recent years, thin film photovoltaics (PV) have attracted the attention of scientific society due to simplicity of manufacturing, yearly increased efficiency and ease of mounting on different surfaces. Thin film solar cell technology is increasing in capacity and market share and now accounts for approximately 20% of the PV market. CdTe solar cells represent approximately half of this market, with the rest being divided between thin film silicon and  $\text{Cu}(\text{In,Ga})\text{Se}_2$  [1]. One limitation still faced by all thin film solar cell technologies is the low light absorption near the band gap edge [2]. This low light absorption is also an issue for CdTe solar cells, which recently increased in efficiency to 20.4% [3]. It is critical to structure the CdTe solar cell such that light can be trapped inside the active layer by increased absorbance. A relatively new method of achieving light trapping in thin film absorber is the application of

metallic nanoparticles that have surface plasmon resonance (SPR). Proper engineering of these structures enables light to be concentrated and ‘folded’ into a thin semiconductor layer, thereby increasing its absorption [2]. This approach would reduce significantly the thickness of thin film solar cells, decreasing demand for scarce semiconductor material as Te, the supply of which limits the scale-up of CdTe solar cells [4].

Combining periodic metal nanostructures on top of ultrathin CdTe layer was theoretically demonstrated to be an effective approach to enhance broadband optical absorption by the CdTe absorber [5]. Among various metals (Ag, Al, Au, Cu) and geometries under investigation (nanodisc (ND), nanosphere (NS)), Al NDs tend to provide the maximum enhancement over the spectral absorption range of interest. The plasmon resonance wavelength of Al ND leads to an optimal localized surface plasmon resonance (SPR) spectrum that maximally matches the intrinsic CdTe absorption profile weighted with the solar spectrum [5].

The optimal parameters of metal nanoparticles (NPs) to enhance the absorption of CdTe absorber were studied theoretically

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[2,5] but yet to our knowledge no experimental data confirmed these results. Moreover, little information is available about suitable technology for the incorporation of metal NPs into CdTe absorber layer. Experience from the technology of Si solar cells with incorporated NPs highlights various methods for the inclusion of NPs in thin film absorbers: sputtering on a one-dimensional sinusoidal grating with a certain period and amplitude [6]; using arrays [7]; evaporation, in which a very thin metal layer is deposited by vacuum evaporation and then annealed so that the metal islands coalesce into metal particles [8]; chemical solution deposition, where the device surface is exposed to a solution containing colloidal NPs and then blown dry [9]; imprint lithography, in which a sol-gel mask is defined by soft lithography using a rubber stamp, followed by metal evaporation and lift-off [10].

This study presents experimental results for a CdTe absorber with incorporated Au NPs. The SPR peaks of gold nanostructures can be tuned from the visible to the near infrared region by controlling their shape and periodicity [11]. The inert nature of gold and the instability of gold oxides at low temperature [12] make gold nanostructures well suited for various applications [11] including CdTe solar cells. One of the first techniques [13] used to prepare gold NPs is the reduction of HAuCl<sub>4</sub> by citrate in water (Turkevich method) [14]. Our experiments were performed using the same HAuCl<sub>4</sub>·3H<sub>2</sub>O reagent solution as a precursor for Au NPs. The Au NPs were incorporated into CdTe layers by spray pyrolysis, spin coating and sputtering methods, and the results from these methods were compared.

## 2. Materials and methods

CdTe thin films with a thickness of ~300 nm were prepared by close spaced sublimation (CSS) onto cleaned soda-lime glass substrates by taking 6N pure CdTe powder (Alfa Aesar) as the source material. The deposition was carried out at a pressure below 2·10<sup>-6</sup> Torr with the source to substrate distance of 0.7 cm. The films were deposited at the source temperature of 550 °C and at the substrate temperature of 300 °C, controlling the temperature through a K-type thermocouple. The deposition lasted for ~1 min, after which the chamber was slowly cooled down to 50 °C.

The Au NPs on the CdTe films were formed by three methods: spin coating, spray pyrolysis and sputtering. The spin coating was carried out with HAuCl<sub>4</sub>·3H<sub>2</sub>O ethanol solution at concentrations: 0.05 M, 0.075 M and 0.1 M at room temperature (RT) in two spin ramp rates: 600 rpm for 5 s and 1200 rpm for 20 s. After coating, samples were dried in air at ~85 °C for 40 min and air annealed on a hot plate at 380 °C for 1 h.

In the case of spray pyrolysis the Au NPs were deposited from the same HAuCl<sub>4</sub> solution on preheated CdTe/glass substrates placed onto a molten Sn bath. The substrate temperature was maintained at 360 °C with an accuracy of ±2 °C. The volume of the spray solution varied from 2.5 ml to 15 ml, while the solution concentration of Au<sup>3+</sup> and the flow rate were kept constant for all CdTe/glass samples: 2 mM and 1 ml/min, respectively. After the coating no drying or annealing was applied for sprayed samples due to enough high temperature for decomposition of AuCl<sub>3</sub>.

In a different approach, a thin film of Au was sputtered for 40–70 s on glass substrate, which was then air annealed at 500 °C for 30 min to coalesce into compact Au grains. The grains were coated with a CSS CdTe film.

All the CdTe–Au layers were characterized by X-ray diffraction (XRD), optical transmission and reflection spectra, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). XRD measurements were collected with a Rigaku Ultima IV diffractometer with Cu K $\alpha$  radiation in the Bragg–Brentano ( $\theta$ – $2\theta$ ) geometry. The crystallite size and lattice parameters were

calculated using the PDXL Version 1.4.0.3 software on the Rigaku system. The optical total transmittance and reflectance spectra of the films were measured in the wavelength range of 200–2500 nm on a Jasco V-670 UV–VIS–NIR spectrophotometer equipped with an integrating sphere. A high resolution SEM apparatus (Zeiss EVO-MA15) was used at a 10 kV operating voltage, while the elemental composition was analyzed by EDX with the Röntec EDX XFlash 3001 detector and the Oxford Instruments INCA Energy system.

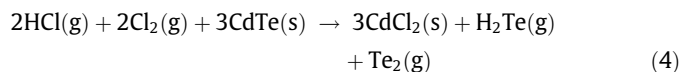
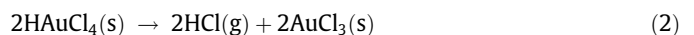
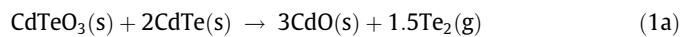
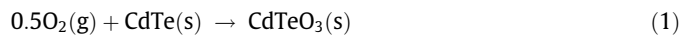
## 3. Results and discussion

### 3.1. Spin coated Au solution on CdTe layer

Spin coating of HAuCl<sub>4</sub> on CdTe layers and subsequent annealing in air at 380 °C resulted in Au NPs and wires binding the NPs as a web and covering the surface of CdTe layer (Fig. 1). We assume that these wires represent the residual cadmium oxychloride (2CdO·CdCl<sub>2</sub>) created in the air annealing process [15] as an intermediate product of the HAuCl<sub>4</sub> reaction with CdTe [16]. From SEM images, the mean size and spacing of Au NPs were estimated as on the order of 100 nm and 300 nm, respectively.

The SPR valley at 577 nm in the transmittance spectrum of the CdTe–Au layer (Fig. 2a) confirms the plasmonic absorption resonance of incorporated Au NPs. However, this effect did not lead to a noticeable enhancement in the absorption over the entire wavelength range (Fig. 2b). Moreover, reflectance and transmittance spectra show the disappearance of the CdTe absorption edge in the 800 nm region (Fig. 2a) indicating the removal of the CdTe film in the spin coating process.

To understand the disappearance of the CdTe band edge (Fig. 2), we analyzed the reactions that may take place in the air annealing process of the CdTe layer with spin coated HAuCl<sub>4</sub> solution: oxidation of CdTe to CdTeO<sub>3</sub> (CdO·TeO<sub>2</sub>) (1), decomposition of HAuCl<sub>4</sub> (2, 3), and formation of CdCl<sub>2</sub> and Te<sub>2</sub> (4). These reactions may form the viscous phase of CdTe + CdTeO<sub>3</sub> + CdCl<sub>2</sub> flux [15,17], which has a low melting temperature (<400 °C).



We carried out some calculations to evaluate the impact of the CdCl<sub>2</sub>-containing flux on the CdTe film after coating with the HAuCl<sub>4</sub>·3H<sub>2</sub>O solution. Au NPs with both a diameter and spacing of 50 nm (minimal values for a 2% absorption enhancement [18]) cover 0.4 of a 1 cm<sup>2</sup> CdTe film surface. Based on the mass of gold, the amount of gold in the HAuCl<sub>4</sub> solution was calculated as 1.32·10<sup>-5</sup> mol. As each mole of HAuCl<sub>4</sub> yields two moles of CdCl<sub>2</sub>, a 1 cm<sup>2</sup> CdTe film will contain 2.65·10<sup>-5</sup> mol of CdCl<sub>2</sub>. Therefore, the mass ratio of CdCl<sub>2</sub> (created by HAuCl<sub>4</sub>) to CdTe is at least 25. Considering the solubility of CdTe in the CdCl<sub>2</sub> flux (~25%) [19], it is highly likely that the CdTe film will disappear. Therefore, though the RT spin coating of Au NPs from HAuCl<sub>4</sub> solution on CdTe layers is a very simple technique, it should be discarded due to the substantial removal of CdTe by the reactions with chloride flux in the annealing process.

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