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Nanowire and Core-Shell Structures on Flexible Mo Foil for CdTe Solar Cell Applications.

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Abstract

CdTe films, nanowires, film-nanowire combinations and CdS-CdTe core-shell structures have been fabricated in a preliminary survey of growth methods that will generate structures for PV applications. Selectivity between film, nanowire and film plus nanowire growth was achieved by varying the pressure of N₂ gas present during Au-catalysed VLS growth of CdTe, on either Mo or Si substrates. Metamorphic growth of CdTe nanowires on sputtered CdTe films, deposited on glass substrates, was demonstrated. Coating of CdTe nanowires with CBD CdS gave conformal coverage whereas coating with MOCVD (Cd,Zn)S yielded highly crystallographic dendritic growth on the wires.

Introduction

In the search for high performance, low-cost solar cells, novel device structures are being explored. By using arrays of vertical nanowires instead of thin films within a device, the traditional planar p-n junction may be replaced by a number of radial junctions. In this geometry, the distance that generated carriers must migrate can be made shorter than minority carrier diffusion lengths, and electron-hole recombination may consequently be reduced. As a result, the constraints on the quality and purity of the active semiconductor material may be lowered [1]. The design orthogonalises carrier separation and light absorption so structures can still be grown thick enough to absorb the sunlight [2]. Indeed, Si wire arrays have been observed to capture as much light as traditional wafer based devices, whilst using 1/100th the material [3].

Despite the large presence of CdTe in the field of photovoltaics, little has been reported

of CdTe nanowire based solar cells. Kang *et al.* spin coated poly(3-octylthiophene) onto electro-deposited CdTe nanowires, and achieved device efficiencies of 1.06% [4]. Using a different approach, Fan *et al.* encapsulated n-type CdS nanopillar arrays within a thin film of p-type CdTe and demonstrated the system's potential by obtaining 6% efficiency [5].

We present successful growth of Au-catalysed CdTe nanowires on Mo and Si substrates by the VLS method. It is shown that the balance between the formation of layers (i.e. two-dimensional growth) and of nanowires (one-dimensional growth) is influenced by the pressure of inert gas present during growth. Deposition of CdS and of (Cd,Zn)S in view of constructing the aforementioned radial p-n junctions is demonstrated. Layer-wire combinations and core-shell structures are reported, as are preliminary attempts to make complete devices with sputtered ITO front contacts.

Experimental

0.1 mm thick Mo (99.9% purity) and 0.314 mm thick Si <111> substrates were used in the investigation. For each, 15 mm x 15 mm samples were cut, scrubbed with de-ionised water and blow dried using N₂. Au films (~ 4 nm) were thermally evaporated onto the substrates and then annealed at 360°C for 30 minutes to form arrays of nano-sized spherical drops. Annealing and growth steps were carried out in the chamber of the close space sublimation (CSS) kit. Substrates were held 10 mm above a powdered CdTe source (99.999%, Alfa Aesar). For optimum nanowire growth, CdTe was deposited for 30 minutes under a N₂ pressure of 25 Torr with

the source and substrate held at 570°C and 520°C respectively.

Cd_{0.9}Zn_{0.1}S window layers were grown on some of the samples by the horizontal MOCVD method at a substrate temperature of 360°C under atmospheric pressure, with H₂ used as the carrier gas. The precursors employed were dimethylcadmium (DMCd), ditertiarybutylsulphide (DtBS) and diethylzinc (DEZn), supplied by SAFC Hi-Tech. Film thickness, which was in the range 200-600 nm in this study, was monitored and controlled in-situ by laser reflectometry.

On the remaining samples, CdS window layers were deposited by chemical bath deposition. The process used CdSO₄ with NH₄OH at 70°C with thiourea being added and deposition taking place for 9 minutes [6].

RF sputtering was used to deposit ITO as a transparent front contact to complete the device structures. The ITO (99.99%, AJA) was sputtered at 60W onto the substrates, held at 250°C, under an Ar pressure of 1 mTorr for 2 hours. This generated layers, having a sheet resistance of 10 Ω/□.

Results and Discussion

Nanowires and the effect of growth conditions;

An array of Au-catalysed CdTe nanowires grown on Mo is shown in Fig. 1a. The wires had diameters in the range 100-500 nm, these being considered to be governed by the Gaussian distribution of the Au catalyst drop diameters [7], measured for these samples from electron micrographs. Typically the thinner wires were observed to grow to greater lengths, some exceeding 20 μm, than the thicker wires. This suggests that the diffusion of adatoms from substrate to catalyst is the predominant contribution to nanowire growth, rather than the direct adsorption of atoms, as reported by Dubrovskii *et al.* [8]. Energy dispersive X-ray (EDX) spectroscopy taken from the stem of a nanowire was dominated by Cd and Te Lα1 peaks as expected. EDX also confirmed that the Au catalyst remains at the tip of the nanowire, proving that growth was via VLS, as shown in Fig. 1b. Using similar conditions, nanowire growth was also demonstrated on Si substrates.

The growth mechanism here is atypical of standard VLS growth however. A rough, thin film of CdTe, ~ 500 nm, was established on the substrate before one-dimensional growth began. This initial film was directly observed in cross sectional SEM images. Furthermore, much shorter deposition times yielded a layer but no nanowire growth. The lattice mismatch of this system is very high (lattice parameters $a = 0.648$ nm and 0.315 nm for CdTe and Mo

respectively) and so the resultant strain initially prevents coherent one-dimensional growth. Chuang *et al.* demonstrated that the critical nanowire diameter, above which coherent VLS growth cannot occur, is extremely small (of the order of a few nm's) for highly mismatched systems [9]. Once a thin film of CdTe has established however, it effectively becomes the substrate of the system and there is no longer a mismatch, and one-dimensional growth becomes favourable (illustrated in the schematic diagram in Fig. 1c). Cross sectional SEM imaging also confirmed that some of the smaller Au particles became trapped under the initial layer, whereas others rise to the surface and nucleate wire growth.

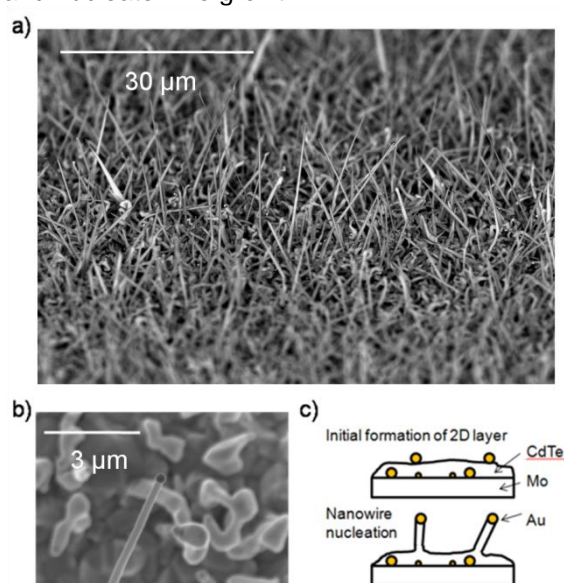


Figure 1: (a) SEM image of an array of CdTe nanowires on a Mo substrate (20° tilt) (b) SEM image of a single nanowire. (c) Illustration of the growth mechanism.

The nanowires in Fig. 1 were grown under a N₂ pressure of 25 Torr. However, when the pressure was increased to 150 Torr, it was observed that two-dimensional films formed instead (Fig. 2). This may be explained in terms of the VLS growth mechanism, which is only considered to proceed when the catalyst drop is saturated with dissolved CdTe. High pressures of buffer gas inhibit transport of CdTe to the catalyst drop, the required supersaturation is not achieved and growth proceeds to form a layer but not nanowires. The degree to which layer or nanowire growth is favoured may therefore be controlled by adjusting the pressure of N₂ gas in the chamber, with low pressures (e.g. 10 Torr) encouraging surface diffusion control and the growth of wires up to 100 μm in length.

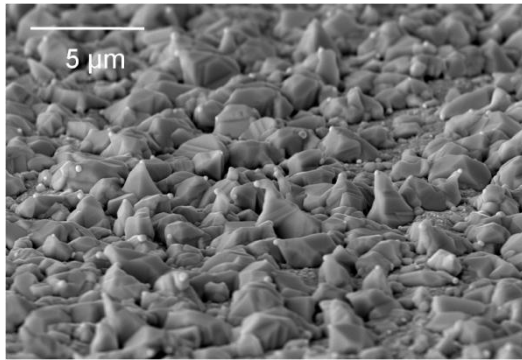


Figure 2: Two-dimensional film formed under 150 Torr N_2 . CdTe was deposited for 30 minutes at $T_{\text{source}} = 570^\circ\text{C}$, $T_{\text{sub}} = 520^\circ\text{C}$.

For close-space sublimation, by increasing the source temperature, the growth rate increases. Consequently, denser arrays of longer nanowires were achieved when $T_{\text{source}} = 600^\circ\text{C}$. However, at a higher substrate temperature (540°C) the density of nanowire arrays reduced because greater surface diffusion lengths enabled adatoms to migrate to established nanowires.

Fig. 3 plots average nanowire height and length as a function of growth time, and therefore illustrates how these dimensions developed. Initially, the diameter remained constant and the length increased roughly linearly with time. The growth rate of the nanowire length decreased after 40 minutes however, coinciding with an increase in diameter. This onset of lateral growth occurred when the length of nanowires began to exceed the surface diffusion length and adatoms were thus unable to reach the catalyst.

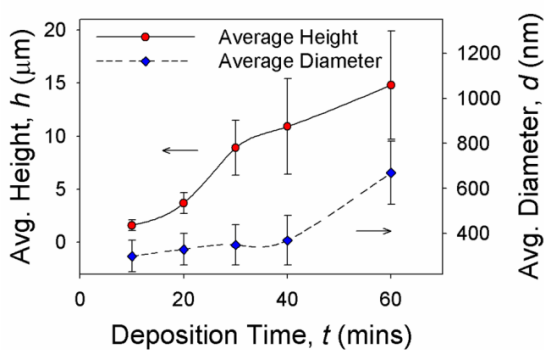


Figure 3: Development of average CdTe nanowire length and diameter over time, for growth under 25 Torr of N_2 .

Core-shell structures;

Fig. 4 is an image of a CdTe nanowire coated with ~ 300 nm of MOCVD-grown (Cd,Zn)S. For photovoltaic applications, a uniform, conformal coating is desirable. However, dendritic growth is observed; a

second generation of nanowires have formed perpendicular to the core CdTe structure. There are three rows of secondary nanowires, with each row displaced 120° around the circumference of the CdTe nanowire to the next. TEM analysis revealed that the CdTe nanowires favoured growth in the $[111]$ direction and so these three rows correspond to growth in the $\langle 110 \rangle$ directions. The crystallographic nature of the growth was further enhanced by longer growth times.

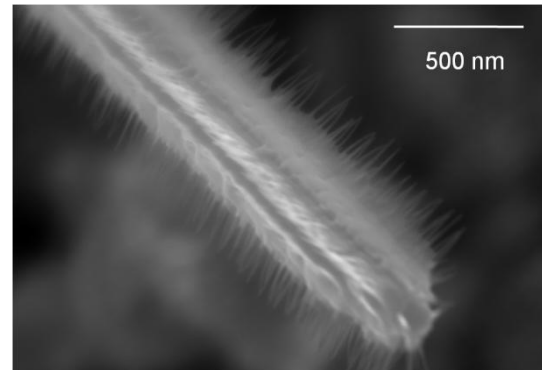


Figure 4: CdTe nanowire coated with MOCVD-grown (Cd,Zn)S. The deposit is dendritic and is crystallographically controlled.

An alternative approach to coating the CdTe nanowires was that of CBD. Fig. 5 shows the improved uniformity obtained with this method. For this sample, a Si substrate was used. The back-scattered electron image reveals compositional contrast, clearly showing a conformal 50 nm CdS shell layer. However, it was observed that a number of the CdTe nanowires collapsed following CBD, whereas there was no such problem for MOCVD.

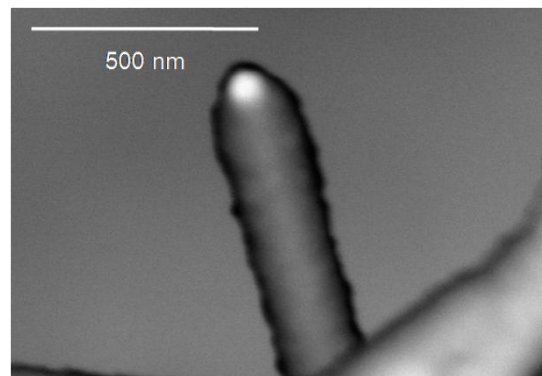


Figure 5: Back scattered electron image of a CdTe/CdS core-shell structure. CdS was deposited by CBD. The Au catalyst shows up as a bright spot.

Preliminary device structures were fabricated by coating the core-shell structures with ITO. 200 nm of ITO was sputtered onto

both the CdZnS/CdTe(NW)/Mo and CdS/CdTe(NW)/Si structures as a transparent front contact. I-V measurements were made for both devices. An ohmic response was observed for the ITO/CdZnS/CdTe(NW)/Mo device, pointing to insufficient coverage of one of the layers, which had enabled shunting pathways to short circuit the device. The evidently non-uniform CdZnS shell layer is likely to be the cause of this. Rectifying behaviour was observed for the ITO/CdS/CdTe(NW)/Si device, but quantum efficiency measurements showed photo-response in the range 400-1100 nm. From this, it was inferred that a CdS/Si junction had been created, once again a result of insufficient coverage of the substrate.

Improving surface coverage;

The failure of both of these devices highlights the necessity for a completely continuous absorber layer. To achieve this, a metamorphic approach for growing CdTe nanowires was attempted, initially on a glass substrate. A 1 μm CdTe film was sputtered onto soda lime glass at 250°C using a power of 70 W. CdTe nanowires were subsequently grown on this film using the optimised CSS conditions described above. Greater nanowire densities were obtained using this approach (Fig. 6), presumably because no catalyst droplets were buried as in Fig. 1c. The sputtered film provides two advantages. Firstly, it acts as a buffer layer and complete coverage of the underlying substrate is achieved. Secondly, it promotes more coherent nanowire growth, as the CdTe film itself becomes the 'substrate' within the vapour-liquid-solid model.

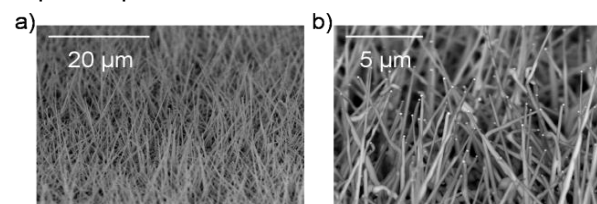


Figure 6: (a) Nanowire array deposited at $T_{\text{source}} = 570^\circ\text{C}$, $T_{\text{sub}} = 520^\circ\text{C}$ under 25 Torr for 20 minutes on a pre-sputtered 1 μm CdTe film on soda lime glass. (b) Back-scattered electron image.

Continued work will aim to incorporate this metamorphic technique into the device fabrication method. We hope to establish a baseline performance for a CdTe nanowire solar cell, from which optimisation experiments can proceed.

Conclusion

A study of the morphological control of CdTe layers, layer-nanowire combinations and CdS/CdTe core-shell structures has been presented. It was demonstrated for VLS growth of CdTe, using Au catalysts, that nanowire growth was encouraged by the use of low pressures of N_2 (e.g. 10 Torr), whereas high pressures (e.g. 150 Torr) favoured the formation of rough two-dimensional films. This was interpreted in terms of suppression of the catalyst supersaturation condition for VLS growth under high pressure of N_2 .

While selection of an optimum N_2 pressure allowed for the formation of nanowires on a semi-continuous film of CdTe, it was found that VLS growth on a seed layer of sputtered CdTe gave films with superior continuity and higher densities of nanowires.

Coating of the wires with CBD-grown CdS yielded conformal coverage, whereas MOCVD-growth of CdZnS yielded highly crystallographic, non-uniform coverage.

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