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# Epitaxial CdTe Rods on Au/Si Islands from a Molecular Compound

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Cadmium telluride (CdTe) is an important infrared direct band gap semiconductor (e.g., ∼1.6 eV, 827 nm, 300 K)[1] and is potentially useful in catalysts,[2] photovoltaics,[3] phosphors,[4] biological tagging,[5] and light-emitting diodes.[6] Several solution- and gas-phase techniques have been used for the deposition of CdTe nanostructures.[7] Due to the strong confinement of charge carriers in CdTe nanocrystals, they have enhanced nonlinear optical properties which can also be useful in opto-electronics.[8]

The deposition of CdTe films by MOCVD generally involves the use of dimethylcadmium and a dialkyl telluride.[9] There exist some reports of the formation of cadmium sulfide/selenide or zinc sulfide as one-dimensional (1D) nanostructures using single-source precursors.[10] These nanomaterials have been prepared with the aid of a metal catalyst by a vapor−liquid−solid (VLS) process. Single-source precursors (SSPs) and CVD offer a number of potential advantages in material delivery as compared to laser ablation or thermal evaporation of bulk materials. These include low-temperature deposition using simple experimental setups which can give better control of the reaction, with a potential for scaling and potentially high quality material. There are no reports on the growth of 1D epitaxial CdTe nanostructures using an SSP route, without the need for a catalyst.

Herein, we report the atmospheric pressure CVD of $Cd[(TeP^iPr_2)_2N]_2$[11a] leading to anisotropic CdTe structures on unmodified $Si/SiO_2$ (100) surfaces. This is the first report of such structures by CVD involving an SSP, and perhaps more importantly without any growth directing additives. In addition, growth on Au-coated surfaces leads to highly unusual clusters of CdTe rods forming on Au/Si islands. The relatively air- and moisture-stable homoleptic compound $Cd[(TeP^iPr_2)_2N]_2$ was synthesized by a recently reported method.[11b] The related complex $Sb[(TeP^iPr_2)_2N]_2$ has been successfully employed in aerosol-assisted (AA) CVD to deposit $Sb_2Te_3$ thin films.[11c,d] Thermogravimetric analysis of the Cd complex under nitrogen showed a single-step weight loss at ∼360 °C with a residue of 22% corresponding to bulk CdTe (calcd 21%).

Initial deposition studies were carried out in a quartz tube heated within a tube furnace on unmodified $Si/SiO_2$ substrates. The precursor was placed upstream of the substrates where the lower temperature (*ca.* 280 °C) volatilized the precursor without significant decomposition. Growth was carried out at atmospheric pressure between 700 and 900 °C, for 15 min, under a dynamic argon flow (300 sccm). The films had good coverage on the substrates but lacked continuity. X-ray powder diffraction (XRD) of the deposited materials showed predominantly cubic CdTe (ICDD No. 01-089-3053) with some evidence for hexagonal (ICDD No. 04-003-4983) material (Figure 1a). This observation is not surprising as the energy differences between hexagonal and cubic forms in chalcogenide systems are small (*ca.* 9 meV/2 atom).[12] Investigations by SEM (Figure 1c, d) revealed rods with diameters ranging from 0.25 to 0.65 $\mu$m and the lengths vary from 0.5 to 2.2 $\mu$m, together with bipodal and tripodal structures. The aspect ratios are *ca.* 5.3:1 (nanorods), 5.4:1 (bipods), and 3.3:1 (tripods). The horizontally grown rods and pods are randomly distributed over the substrate surface, with a complete absence of significant two-dimensional planar growth.

The results of SEM studies are consistent with individual crystallites containing both cubic seeds (tetrahedra) and hexagonal rods consistent with the XRD results.[13] Quantitative EDAX measurements carried out during SEM imaging confirmed the 1:1 stoichiometry of the CdTe structures. No impurities such as phosphorus or nitrogen are seen in the EDAX spectrum. Therefore, under controlled experimental conditions, it is possible to grow CdTe nanorods and nanopods on bare-oxidized Si substrates without the need of any metal catalyst or surface preparation.

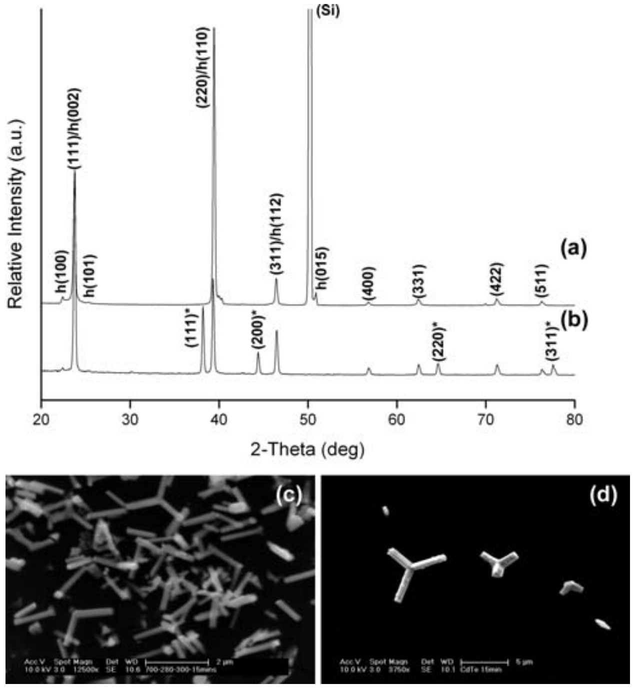

***Figure 1.*** XRD of CdTe deposited on (a) $Si/SiO_2$ (100) and (b) Au−$Si/SiO_2$ (peaks marked by asterisk are gold; *h* indicates hexagonal features). (c,d) SEM images of CdTe crystals on $Si/SiO_2$ substrates at 700 °C.

During the experiment, the precursor is decomposed in the hot-walled reactor to form CdTe nanocrystallites, promoting the self-seeded growth of rods and pods even on the bare $Si/SiO_2$ substrate. The possible reason for forming different structures is that zinc-blende type cubic nuclei are not identical in all four facets where crystals start their growth.[14]

The $Si/SiO_2$ substrates sputtered with gold layers were also investigated for the growth of CdTe structures. The Au/Si system is known to exhibit an extremely low eutectic temperature (363 °C)[15]

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which consequently leads to the formation of Au/Si islands on the substrate surface. The formation of a molten semiconductor-metal alloy serves as a preferential site for the epitaxial growth of rods on a substrate due to the high sticking coefficient of the molten alloy. When deposition occurs on this substrate, this mechanism determines the diameter and growth rate of the rods.[16] The XRD (Figure 1b) confirmed the presence of CdTe and elemental gold. The method gave rods that are highly uniform in diameter. These CdTe rods appear to be shorter in length, but their lateral growth has significantly increased (to 0.63 $\mu$m). At higher deposition temperatures, larger Au/Si islands grow at the expense of smaller ones (Ostwald ripening) due to an increase in the mobility of Au on the surface. One parameter of crucial importance in this context, especially for epitaxially grown rods, is the crystallographic growth direction. Further investigation into the angle of growth confirms epitaxial growth at 90°, 54°, and 45°, being consistent with the growth angle expected of rods growing out of the Si (100) plane along the (110) axis (45°), (111) axis (54.75°), and (100) axis (90°).[17] As depicted schematically in Figures 2 and S1, the CdTe rods are unambiguously (110)-oriented, with further evidence of growth along the (111) and (100) planes being identified due to the orientation visible in SEM which is consistent with the preferential orientations observed by XRD. The TEM shows a *d* spacing of 0.13 nm, which is consistent with the cubic (111) plane of CdTe (Figure S2).

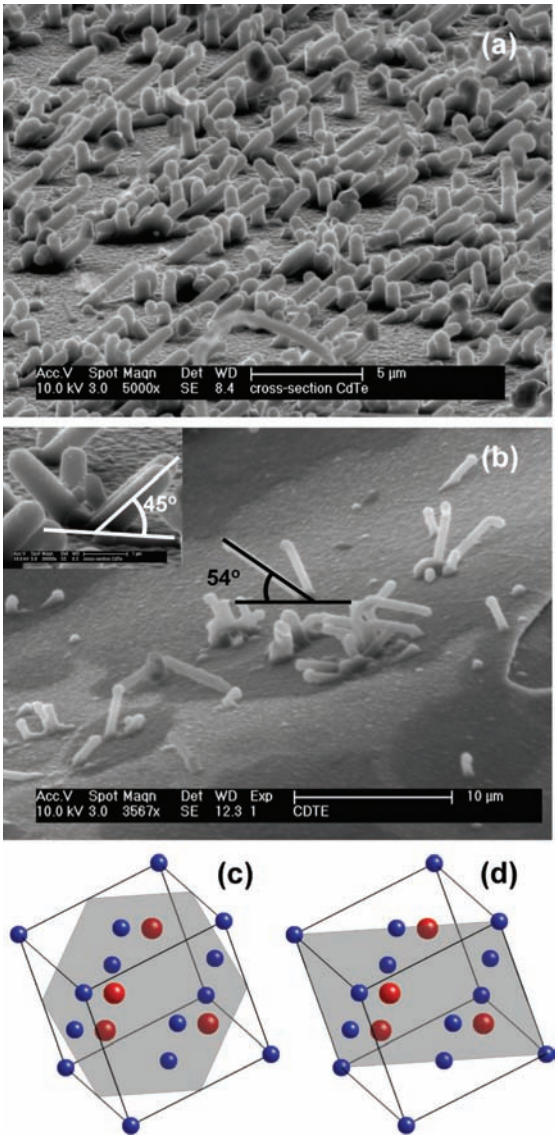

***Figure 2.*** SEM images of rods grown (a) on Au/Si islands and (b) along (111) plane. Inset shows growth along (110) plane. (c and d) Schematic illustrations of growth planes in cubic CdTe.

Although Au-sputtered substrates were used for deposition studies, there was no evidence of Au-capped particles at the tips of the crystallites. Growth of the CdTe structures is therefore unlikely to have taken place by a VLS mechanism. It is more likely that the growth is induced by a vapor−solid (VS) process. The resulting Au/Si islands have a large accommodation coefficient and are therefore a preferred deposition site for incoming CdTe atoms from the vapor phase.[18] After the Au/Si alloy becomes supersaturated with CdTe atoms, the nucleation and growth of nanorods are initiated. Again, EDAX analysis of the rods showed stoichiometric cadmium telluride.

The significance of the current study is twofold. First of all, we have utilized the homoleptic cadmium compound $Cd[(TeP^{i}Pr_2)_2N]_2$ for the growth of anisotropic CdTe structures on bare $Si/SiO_2$ substrates. To the best of our knowledge, SSPs have not been previously studied for the generation of CdTe nanorods or -pods from the vapor phase. Secondly, clusters of highly uniform CdTe rods are grown on Au/Si islands as opposed to VLS growth of Au-capped rods.

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**Supporting Information Available:** Experimental procedure, a SEM and HRTEM of a CdTe rod are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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