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Optical properties of mesoporous II–VI semiconductor compound films

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Direct liquid crystal templating from non-ionic polyoxyethylene surfactants has been utilised to produce well-defined bi-refringent films of nanostructured cadmium telluride films which displayed good optical properties as evidenced by UV/VIS reflectance spectroscopy.

Nanostructuring of materials is now a clear route to optimise and elicit new functional properties. In particular nanostructured semiconducting films with one or more critical dimension in the nanometer range possess novel electronic and optical properties in comparison to their non-mesoporous counterparts. Such materials are of considerable fundamental and technological interest for understanding the fundamental physics of low-dimensional structures and to applications in sensors, optical devices and solar cells because they are entirely composed of surface atoms. As a consequence these materials should exhibit unusual charge carrier dynamics, improved collection of the photogenerated carriers and hence solar conversion efficiencies. In this respect cadmium telluride (CdTe) is one of the most attractive materials because of its direct bandgap of 1.44 eV[1] which provides an optimal match with the solar energy spectrum. This makes it ideally suited as a component of devices for solar energy conversion. The electrochemical route[2–6] is particularly promising for low-cost large-scale production of photovoltaic cells, and CdTe prepared in this way is a striking example of the high quality semiconducting materials that can be obtained by electrodeposition. The ability to electrodeposit mesoporous nanostructured semiconductors highlights the possibility of creating a new class of materials that exhibit unusual electronic and optical properties.

It has recently been demonstrated that lyotropic liquid crystalline (LC) mesophases of non-ionic surfactants can act as nanoscale templates for the electrochemical growth of films of adherent high-quality metal (*e.g.* platinum, silver, cobalt)[7] and elemental semiconductor (*e.g.* tellurium and selenium)[8–9] films leading to well-defined periodic three-dimensional interconnected nanostructures. We report here the first synthesis of uniform and high-quality II–VI semiconductor compound films of CdTe with a hexagonal nanoarchitecure fabricated *via* this direct liquid crystal templating route. The preparation of the nanostructured mesoporous CdTe films was carried out by cathodic electrochemical co-deposition of cadmium sulfate and tellurium dioxide dissolved in the aqueous domain of the hexagonal lyotropic liquid crystalline phase (H_I) of the non-ionic surfactant octaethyleneglycol monohexadecyl ether ($C_{16}EO_8$). We employed plating mixtures comprising aqueous solutions of 0.15 M $CdSO_4$ and 0.005 M TeO_2 dissolved in 2 M sulfuric acid mixed in a 1 : 1 ratio with 50 wt% of $C_{16}EO_8$ in de-ionised water. The optical texture of the plating mixtures was routinely examined under a polarizing optical microscope and reproducibly revealed a normal topology hexagonal mesophase which was found to be stable up to a temperature of 65 °C. Electrodeposition of the CdTe films was conducted onto evaporated gold on glass films and was achieved under potentiostatic control. The deposition potential was stepped from 0 V to between −0.54 V and −0.65 V relative to a saturated calomel electrode (SCE) at a constant temperature of 25 °C. To grow visibly thick films of CdTe suitable for structural characterization by TEM and XRD, the potential was stepped from 0 V to −0.58 V *vs.* SCE with deposition times varying between 5–16 h. Post-deposition treatment of the electrodeposited CdTe films (denoted H_I-eCdTe) involved soaking in water for at least 24 h. During this period the water was replaced every 2 h until all of the surfactant was removed. The films were then allowed to dry under ambient conditions in air. The H_I-eCdTe deposits were typically grey and shiny in appearance and exhibited a uniform optical texture. CdTe films (denoted eCdTe) were also deposited under the same conditions in the absence of surfactant for reference.

The long range mesoporosity of the mesoporous CdTe films was investigated by using low angle X-ray scattering, while TEM was employed to provide direct evidence of the existence of a nanostructure. Low angle XRD was performed between 1° and 4° in 2θ (Cu–Kα radiation) and one main diffraction peak (d_{100}) was observed at 1.52° which can be assigned to diffraction from a hexagonal lattice with a lattice parameter of 69 ± 1 Å. A peak was not observed for the reference CdTe films deposited in the absence of surfactant. Wide angle XRD spectra of the as-deposited films CdTe films revealed a strong preferential orientation along the $<111>$ direction.

Direct evidence of the existence of a nanostructure for the electrodeposited films was obtained by TEM. Fig. 1 shows a TEM micrograph displaying a hexagonal array of cylindrical pores with an average pore-to-pore distance of 70 ± 2 Å at the point of nearest contact between neighbouring channels. These values are in good agreement with the XRD results.

We can control the stoichiometry of the CdTe films by controlling the deposition potential over the range −0.4 to −0.8 V *vs.* a saturated calomel reference electrode (SCE) as evidenced by EDX. In this way we were also able to exercise control over their optical properties.

In order to characterise the suitability of the films for optical/optoelectronic applications we have measured their optical reflectance spectra as shown in Fig. 2.

These measurements show strong interference fringes, which clearly indicate the optical flatness of the films. In addition the

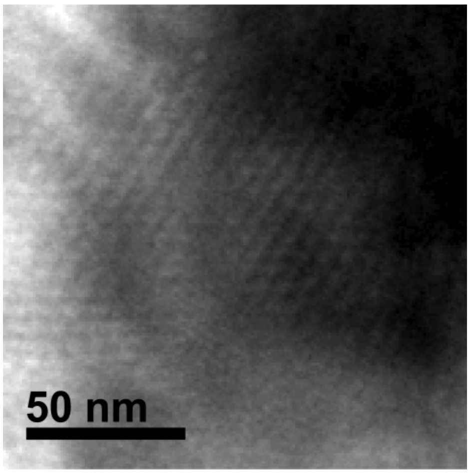

Fig. 1 Transmission electron micrographs of CdTe electrodeposited from the hexagonal liquid crystalline phase of $C_{16}EO_8$ at 25 °C with an end-on view of the pore structure.

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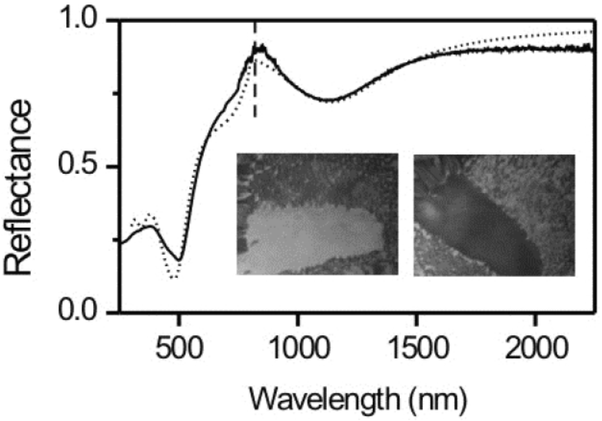

Fig. 2 Reflectance spectra (solid line) of a stoichiometric, as determined by EDX, mesoporous CdTe film compared to a simulated spectrum (dotted line) determined from the model discussed in the text. The insets are optical micrographs of a mesoporous CdTe film with cross polarised illumination and observation before and after a rotation of the sample by 45°. They show a large domain, longest dimension ≈ 1 mm, which changes from dark to light upon a 45° rotation clearly indicating the sample's birefringence. The dashed line indicates the value of the room temperature bandgap, 860 nm, of non-mesostructured CdTe.

optical measurements indicate that the onset of absorption in the films is strongly dependent on their composition, with the onset of absorption for stoichiometric films occurring at close to the accepted room temperature bandgap, 858 nm, of CdTe. We have performed some initial modelling[10–12] of the films assuming that the dielectric coefficient is a volume weighted average of the dielectric coefficients of CdTe and air; this assumption is correct if the electric field of the light is parallel to the pores. Considering the simplicity of the model, it is remarkably close to the experimental results. Due to the strongly anisotropic shape of the pores one would expect the films to exhibit form birefringence; with the dielectric coefficient for the electric field perpendicular to the pores being smaller than that for the orthogonal case. The birefringent nature of the films is clear when they are observed using a standard metallurgical microscope with crossed polarised illumination and observation (see inset to Fig. 2 where the large domain is observed to change from light to dark when the sample is rotated by 45° under the microscope).

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