

# CdTe Nanocrystal Synthesis in SiO<sub>2</sub>/Si Ion-Track Template: The Study of Electronic and Structural Properties

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The synthesis of CdTe nanocrystals (NCs) is performed by electrochemical deposition into prepared ion tracks in a a-SiO<sub>2</sub>/Si-n template. As a result, CdTe NCs are obtained in a wurtzite (WZ) crystal phase. The measurement of the current-voltage characteristics shows that the CdTe (WZ NC)/SiO<sub>2</sub>/Si system obtained in this way has n-type conductivity. Computer simulations using the CRYSTAL computer code show good agreement between experimental and calculated lattice parameters. The theoretical calculations also show that the crystal has a direct bandgap at the  $\Gamma$  point of the Brillouin zone.

## 1. Introduction

Nowadays, the study of various modifications and structures on the base of CdTe—A<sup>2</sup>B<sup>6</sup> semiconductor compound—is of great interest due to its widespread use in solar cells, ionizing radiation detectors, and photocells.<sup>[1–4]</sup> However, the difficulties of managing the electronic properties and purity-defect ensemble of CdTe limit its wide practical use. Therefore, the study and development

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of technologies for stable growth and doping CdTe thin films and nanostructures (nanocrystals [NCs], nanowires, and so on) continue to remain relevant.

There are many ways to obtain CdTe, ranging from simple to complicated multistage procedures.<sup>[1,5]</sup> It is well known that crystalline CdTe can exist in four structural modifications: sphalerite, wurtzite (WZ), rock salt, and  $\beta$ -Sn type.<sup>[6]</sup> Some of these modifications can be obtained only at high pressures. In the past years, nanostructures of various substances were obtained using

a a-SiO<sub>2</sub>/Si track template synthesis.<sup>[7–10]</sup> Among a wide variety of different techniques, template synthesis can be put on a special place due to its simplicity, low cost, and high quality.<sup>[7–10]</sup> Ion-track technology is one of the easiest ways to fabricate templates.

As was recently demonstrated for zinc oxide (ZnO) deposition in the a-SiO<sub>2</sub>/Si track template,<sup>[10]</sup> the formation of ZnO NCs is possible in all known phases—WZ, zinc blende (ZB), and rock salt—at different voltages between electrodes. Recently, we synthesized the CdTe NCs into the nanoporous SiO<sub>2</sub>/Si template using the electrochemical deposition (ECD) procedure.<sup>[2]</sup>

In this study, we investigated the conditions of CdTe NC synthesis formed in the a-SiO<sub>2</sub>/Si-n ion-track templates, in the line of influence to structural and electronic properties. Accordingly, the quantum chemical calculations of lattice parameters and the electronic properties were carried out.

## 2. Experimental Section and Results

The silicon dioxide (SiO<sub>2</sub>) film,  $\approx$ 700 nm thick, was thermally grown on the n-Si (100) wafer. The SiO<sub>2</sub>/Si samples of 5 × 5 mm and 20 × 20 mm were cut from the oxidized Si wafer. To create latent ion tracks in the SiO<sub>2</sub> matrix, afterward, irradiation was conducted with a 200 MeV Xe up to a fluence of 10<sup>7</sup> ions cm<sup>-2</sup>. It is important to note that the DC-60 accelerator was specialized in the production of nuclear polymer membranes, where ion fluence was varied in a very wide range from 10<sup>5</sup> to 10<sup>15</sup> ions cm<sup>-2</sup>.

Ion tracks were etched in 4% HF aqueous solution with the addition of palladium chloride (PdCl<sub>2</sub>). PdCl<sub>2</sub> concentration in the etchant was  $0.0417 \, g \, L^{-1}$ , and the appropriate etching temperature was  $T = 18 \, ^{\circ} \pm 1 \, ^{\circ}$ C. Before etching the tracks, the corresponding ultrasonic cleaning of the surface of the samples



in isopropanol was conducted for 15 min in an ultrasonic cleaner 6.SB25-12DTS at 80 °C. Cleaning, which was conducted at two frequencies of 25 and 40 kHz, provided sufficient cleaning of the sample surface. After treatment in HF, the samples were washed with deionized water (18.2 M $\Omega$ ).

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Sample surface analysis was conducted using a scanning electron microscope (SEM) JSM 7500F. **Figure 1** shows empty nanopores created by etching (black circles), whereas their transverse cleavage shows their truncated cone shape. The cone rested on the silicon substrate. The conical shape of the pores was due to the comparability in the magnitude rates of the etching of the material in the region of the track Vt and in the volume of the intact matrix Vb.<sup>[11]</sup> The conical shape was confirmed by transmission electron microscope studies<sup>[12,13]</sup> and atomic-force microscope.<sup>[14]</sup>

The ECD)of CdTe was conducted using a solution 1 M CdCl<sub>2</sub> + 1 mM TeO<sub>2</sub>. CdCl<sub>2</sub> was dissolved in water and TeO<sub>2</sub> in a minimal amount of concentrated hydrochloric acid. In hydrochloric acid, this oxide dissolved instantly. The two solutions were combined, and pH was adjusted to 2. The ECD process was conducted in a specially manufactured cell. (Figure 2). Polished copper plates were the electrodes and ECD was conducted using



Figure 1. SEM images of  $SiO_2/Si$  track template: a) A general view of the etched surface, b) enlarged nanopores, and c) cross section of the nanopore.



Figure 2. Cell model for ECD.

**Figure 3** shows SEM images after the ECD of CdTe in a template using a chloride electrolyte at a constant voltage on the electrodes of 1.15 V for 15 min. The left part shows the surface at 4000x magnification, whereas the right part shows the same surface at 50 000× magnification. The black circles are unfilled pores (Figure 1), whereas the white ones are filled. We estimated the degree of the filling of the nanopores to ≈50%. It should be noted that the degree of pore filling depends on ECD time, voltage on the electrodes, as well as the composition of electrolytes. There is also certain dependence on the nanopore diameter. All this, of course, requires a separate study.

X-ray diffraction (XRD) analysis was conducted on a D8 ADVANCE ECO X-ray diffractometer (Bruker, Germany), using an X-ray tube with a Cu anode (Cu K $\alpha$ ,  $\lambda = 0,154$  nm, 40 rV, 25 mA), in the angle range  $2\theta$  of ( $30^\circ$ - $110^\circ$ ), with a step of 0.01° (the time of measurement was 1 s). XRD patterns: voltage -40 kV and current -25 mA. The main distinct peaks measured on the as-deposited sample in the range between 33° and 48° can be attributed to the (102), (110), (200), and (004) planes of WZ CdTe, respectively. The crystal lattice parameters, as well as the dynamics of their changes, were determined using the DiffracEVA v.4.2 software code. The degree of perfection of the crystal structure was evaluated using the TOPAS v.4 code.

**Figure 4** and **Table 1** show the results of X-ray structural analysis conducted after ECD at a voltage of 1.15 V, the deposition duration of 15 min, and at a temperature of 283 K.

It is well known that CdTe belongs to chalcogenides, and it also crystallizes in a cubic lattice of ZB (a = 0.6478 nm, z = 4, space group F43m), metastable hexagonal type of WZ (a = 0.457 nm, c = 0.747 nm, z = 2), and NaCl cubic type (a = 0.549 nm, z = 4), existing at pressures above 2.1 GPa.  $\beta$ -Sn hexagonal type (a = 0.586 nm, c = 0.294 nm, z = 4) is stable at pressures above 10 GPa.<sup>[6]</sup>

A comparison of our experimental parameters with the published data for the unit cell of CdTe WZ (Table 1) indicates quite good agreement.

In case of CdTe, WZ is a metastable phase, which is difficult to obtain under normal conditions.<sup>[15]</sup> Therefore, up to now, efficient solar cells were created on the base of CdTe ZB.<sup>[16,17]</sup> Note that there are only a few studies devoted to CdTe with a WZ structure.<sup>[18–21]</sup> In particular, polycrystalline CdTe WZ films were obtained by ECD in acid solution<sup>[22]</sup> and in alkaline solutions.<sup>[23,24]</sup> It was found that the composition and phase structure depend on the voltage applied to the electrodes. The formation of CdTe NCs in various forms is a rather difficult task. To obtain nanocrystalline CdTe in the form of dots, rods, tetrapods, etc., either the hot injection of organic solvents at high temperatures (up to 200 °C) or the low-temperature (< 100 °C) methods based on an aqueous solution are used.<sup>[19,25]</sup>

During the fabrication of CdTe with branched architectures, it was established that phase control and switching play a very important role to achieve a branched shape.<sup>[25,26]</sup> To obtain branched formation of CdTe NCs, the nucleation of WZ phase is needed. To extract CdTe NCs from the reaction system, the CdTe NC product was washed with the solvent and separated by centrifugation. Further operations provide CdTe NCs useful for manufacture of various types of devices.<sup>[27]</sup> Recent progress







Figure 3. The SEM images of deposited samples, U = 1.15 V, deposition duration t = 15 min, T = 283 K.



**Figure 4.** XRD patterns of of deposited samples, U = 1.15 V, deposition duration t = 15 min, T = 283 K.

 Table 1. The results of XRD analysis after ECD. The calculated parameters are shown in parentheses.

Phase	Structure	Parameters [Å exp. calc. <sup>-1</sup> ]	Degree of crystallinity [%]	Average size of crystallites [nm]
CdTe	Hexagonal	a = 4.54	54.5	11.24
		<i>c</i> = 7.44		
		a = 4.64		
		c = 7.60		

and prospects in this field, focusing on new insights into CdTe NCs synthesized, device fabrication, NC solar cell operation, and how these findings give guidance on optimizing solar cell performance, are reviewed in a study by Xue et al.<sup>[27]</sup>

In our work we have successfully obtained CdTe nanowires with a WZ crystal structure by conventional ECD at room temperature. The resulting CdTe (WZ NCs)/SiO<sub>2</sub>/Si system could be easily integrated into silicon technology.

The appropriate current–voltage characteristics (CVC) obtained for CdTe (WZ NCs)/SiO<sub>2</sub>/Si are shown in **Figure 5**. The following devices, HP 66312A current source and 34401A Agilent (USA) multimeter, were used to measure electrical properties. CVC) were taken from the array of filled nanochannels of  $0.3 \text{ cm}^2$ . A scheme of installation for CVC measuring was as follows: the sample with deposited nanoprecipitates was placed between two metal plates and the part that overlapped was the one where nanochannels were present. Then, the plates were connected to the current source in series connection to the multimeter. All CVCs were conducted using a second-order polynomial fitting.

As mentioned earlier, the initial Si substrate for  $SiO_2$  film growth has n-type conductivity. From the CVC analysis of the obtained CdTe (WZ NCs)/SiO<sub>2</sub>/Si structure, it can be argued



Figure 5. CVC obtained for CdTe (WZ NCs)/SiO<sub>2</sub>/Si.

that this structure shows an electronic type of conductivity. We calculate the specific conductivity of the nanowire arrays using the formula.

$$\sigma = \frac{dI}{dU}\frac{l}{A} \tag{1}$$

where *l* is the nanowire length, approximately corresponding to the thickness of the oxide layer, 700 nm, *A* is the area, and dI/dU is the tangent of the angle of inclination *I*–*U*.

According to the CVC structure (Figure 5), the differential resistance at forward voltage is  $R = \Delta U/\Delta \approx 1 \text{ V/8 mA} = 29.2 \Omega$ .  $A = 2\pi r^2 \approx 2 \times 3.14 \times 137^2 \text{ nm}^2 = 117\,869 \text{ nm}^2$ ,  $\sigma = 700 \text{ nm}/29.2 \times 117\,869 \text{ nm}^2 = 2 \times 10^3 \Omega \text{ cm}^{-1}$ . It is important to note that the CdTe (WZ NCs)/SiO<sub>2</sub>/Si structure possesses one-side conductivity. Thus, such a structure can potentially be used in devices where reverse current is unacceptable or should be negligible.

In addition to experimental studies, we carried out computer quantum chemical calculations of a pure CdTe crystal using the hybrid exchange-correlation HSE06 method<sup>[28]</sup> and the periodic supercell model. The conventional and primitive cells for pure CdTe with a hexagonal lattice are shown in **Figure 6**. The calculations were carried out in the CRYSTAL program.<sup>[29]</sup> The basis sets (BSs) for Cd and Te atoms have been taken from a study by Heyd et al.<sup>[28]</sup>

It is known that for a better description of the crystal electronic structure, it is necessary to accurately determine the total energy







Figure 6. CdTe primitive unit cell (left), the density of states and band structure (right). The horizontal dashed lines on the right indicate the boundaries of the valence and conduction bands.

of the crystal cell.<sup>[30,31]</sup> From well-known theory, the calculation of the total energy within the periodic model of a crystal is not straightforward<sup>[32]</sup> and other studies. By this reason, CRYSTAL program introduced a complex scheme of preliminary analysis and subsequent calculation of a series of crystalline integrals. In our calculations, high convergence tolerances for the Coulomb and exchange integrals were chosen:<sup>[32–34]</sup> for the Coulomb overlap (10<sup>-7</sup>), Coulomb penetration (10<sup>-7</sup>), exchange overlap (10<sup>-7</sup>), first exchange pseudo-overlap (10<sup>-14</sup>).

The force gradients with respect to atomic coordinates and lattice parameters were evaluated analytically. The equilibrium structure was determined using a quasi-Newton algorithm with a Broyden-Fletcher-Goldfarb-Shanno Hessian updating scheme.<sup>[29]</sup> Convergence in the geometry optimization process was tested on the root-mean-square (RMS) and the absolute value of the largest component of both gradients and nuclear displacements. For all atoms, the thresholds for the maximum and the RMS forces were set to 0.000450 and 0.000300 a.u. and those for the maximum and the RMS atomic displacements were set to 0.001800 and 0.001200 a.u., respectively. The effective charges on atoms were estimated using the Mulliken population analysis. The integration over the Brillouin zone in the reciprocal space was conducted within a  $5 \times 5 \times 3$  Pack-Monkhorst grid. As a result, we calculated the lattice parameters (a,c), which are in good agreement with our experimental data (Table 1).

Figure 6 shows the band structure, together with the density of states calculated for the WZ CdTe crystal. The bandgap at the  $\Gamma$  point of the Brillouin zone was obtained as 1.62 eV, very close to the experimental value of 1.6 eV.<sup>[35,36]</sup> Also, as follows from the density of electronic states, the top of the valence band was represented mainly by Te 5p orbitals, whereas the bottom of the conduction band consisted mainly of Cd and Te 5s orbitals. Charge analysis indicates mixed ionic–covalent bonding.

### 3. Conclusion

The ensemble of nanowires composed of CdTe NCs have been synthesized in  $SiO_2/Si$  track templates using ECD at room

temperature from a chloride electrolyte at a constant voltage of 1.15 V and deposition duration of 15 min. The results of X-ray structural analysis have confirmed the formation of CdTe NCs with the WZ structure.

From the current–voltage curve, it was found that the differential resistance at forward voltage  $\sigma$  is  $2 \times 10^3 \,\Omega \,\mathrm{cm^{-1}}$ . It is important to note that the CdTe (WZ NCs)/SiO<sub>2</sub>/Si structure possesses one-side conductivity and can potentially be used in devices where reverse current is unacceptable or should be negligible. The resulting CdTe (WZ NCs)/SiO<sub>2</sub>/Si system could be easily integrated into silicon technology.

In addition to experimental studies, we have also carried out computer calculations of a pure CdTe crystal using the hybrid exchange-correlation HSE06 method and periodic supercell model via CRYSTAL code. The calculated bandgap is 1.62 eV at the  $\Gamma$  point of the Brillouin zone, which is close to experimental value of 1.6 eV. Also, as follows from the density of electronic states, the top of the valence band is represented mainly by Te 5p orbitals, whereas the bottom of the conduction band consists mainly of Cd and Te 5s orbitals. Charge analysis indicates the mixed ionic–covalent bonding.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### Keywords

ab inito calculations, CdTe nanocrystals, electrochemical deposition,  $SiO_2/Si$  track templates

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