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MOLECULAR SIMULATIONS OF INTERACTIONS BETWEEN CdS NANOPARTICLES AND MONTMORILLONITE

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CdS nanoparticles are semiconductors with a band gap about 2.5 eV and having photocatalytic properties for reduction of CO₂. CdS occurs in two different crystal structures (i) as hexagonal greenockite structure and (ii) cubic hawleyite structure. Nanostructured II-IV semiconductors such as CdS possess properties that make them very photosensitive materials. It is well known that the most of the properties strongly depends on the size and shape of nanoparticle [1]. Preparation of CdS nanoparticles was done in [2] by reaction of cadmium acetate and sodium sulphide in presence of cetyltrimethylammonium bromide (CTAB). CTAB molecules were used to control the diameter of CdS nanoparticles and to preserve their photocatalytic properties [3].

Montmorillonite (MMT) is widely used clay mineral in many branches of industry for applications like the intercalation processes, sorption, fillers to polymers, photoluminescence, catalysis and carriers [4]. In this case MMT was used as host matrix for adsorbed CdS nanoparticles on its surface.

Our work is focused on description of mutual arrangement of CdS nanoparticles with CTA⁺ alkylammonium chains and MMT as well as the calculation of interaction energies between each part of these components by molecular simulations methods. These methods are derived on the parameters obtained from experimental measurements and resultant calculated models and their properties are compared with experimental data to obtain the best agreement between them.

Nanocluster of CdS in the shape of sphere with radius 2 nm was created for both greenockite and hawleyite structure based on their crystallographic data. These nanoclusters were surrounded by various amounts of optimized CTA⁺ (10-100, with step of 10 CTA⁺) in the form of monolayer and bilayer arrangement. The optimized alkylammonium chains of CTA⁺ were placed perpendicular to the surface of CdS nanoparticle. The geometry of micelles consisting of CdS nanoparticle and CTA⁺ for monolayer and bilayer arrangement without water molecules were optimized in Universal force field. The charges of CdS for both greenockite and hawleyite nanoparticles were calculated by the QEq method [5]. The optimized micelles were surrounded by water envelope in the form of sphere layer which consist of 1000 water molecules and then whole structure was placed above MMT surface and optimized.

Interaction energies between CdS nanoparticle, CTA⁺, MMT surface and water were calculated for each optimized model. Comparison of sublimation energies for monolayer and bilayer arrangement of CTA⁺ molecules was done. Based on this comparison we suggested that for larger amount of CTA⁺ molecules (>30) bilayer arrangement is preferred. Obtained experimental and molecular

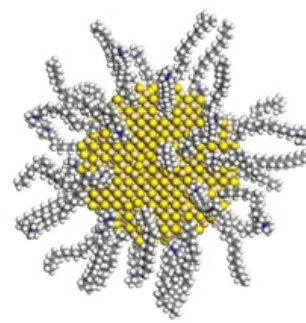


Figure 1. CdS nanoparticle with 40 CTA⁺ molecules in form of bilayer arrangement.

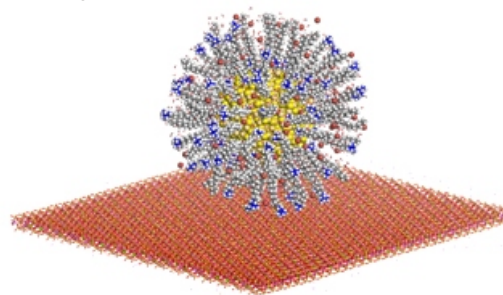


Figure 2. CdS nanoparticle with 100 CTA⁺ molecules in form of bilayer deposited on MMT surface and surrounded by water envelope.

simulation results confirmed that CTA⁺ molecules are able to effectively stabilize CdS nanoparticles forming colloidal dispersions and that the size of CdS nanoparticles can be controlled by the CTA⁺ concentration. Moreover comparison between CdS and ZnS nanoparticles [6] prepared by the same methods was done.

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STRAIN RELAXATION IN GE MICROCRYSTALS STUDIED BY X-RAY DIFFRACTION**J. Rozbořil¹, M. Meduňa¹, C.V. Falub², F. Isa², H. von Känel²**¹*Department of Condensed Matter Physics & CEITEC, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic*²*Laboratory for Solid State Physics, ETH-Zürich, Schafmattstrasse 16, 8093 Zürich, Switzerland
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Monolithical integration of different material layers is increasingly required during fabrication process of modern semiconducting optical and electronical devices. Keeping heterostructures strain and defect free is of course one of the conditions for proper functionality of devices and it could be problematic when materials with different lattice parameters and different coefficients of thermal expansion are matched. Epitaxial growth of layer on a substrate, which lattice parameter does not match with the lattice parameter of the layer, usually leads to a creation of misfit and threading dislocations arising from the interface. Different coefficients of thermal expansion of the layer and substrate causes bowing or even cracks of the heterostructure, when its temperature changes.

A promising method of dealing with those obstacles involves patterning of the substrate into a periodic array of pillars and a deposition with relatively high deposition rate [1]. The resulting heterostructure consists of separated microcrystals grown on the top of each substrate pillar, see Fig. 1. Dislocations created at the interface of layer and substrate are localized only at the bottom part of microcrystals because of high aspect ratio of microcrystals.

In this work, we have studied series of samples of Ge microcrystals deposited by Low-Energy Plasma-Enhanced Chemical Vapor Deposition (LEPECVD) on a Si substrate, which was patterned into the rectangular array of 8 μm tall square based pillars using conventional photolithography and deep reactive ion etching. The studied samples differed in the lateral size of Si pillars varying from 2 μm to 15 μm , and in the size of the trench between two neighbouring Si pillars varying from 1 μm up to 50 μm for different samples.

For the analysis, we have used home assembled diffractometer with a Cu X-ray tube equipped with a Göbel parabolic graded multilayer mirror and a 4-bounce Ge(220) crystal monochromator, providing Cu K α radiation on the incident beam, and an analyzer crystal on the diffracted beam in order to perform high resolution X-ray diffraction measurements using reciprocal space mapping

around symmetrical (004) and asymmetrical (224) diffraction.

We have proved by analyzing diffraction peak positions and their intensity that the Ge forming microcrystals is completely relaxed up to the lateral size of 9 μm whereas the Ge deposited into the trenches is tensile strained.

In order to investigate the dependency of the Ge layer crystal quality on the structure parameters of the substrate patterning, we have analyzed Ge diffraction peak half-widths as well. We have found that the thermal strain plays a dominant role in the diffraction peaks broadening. The diffraction peaks are narrowing with decreasing trench size probably due to the reduction of the areas of the Ge microcrystals extending Si pillars. The samples with 5 \times 5 μm^2 sized Si pillars exhibit the most significant lattice bending from all of the measured samples.

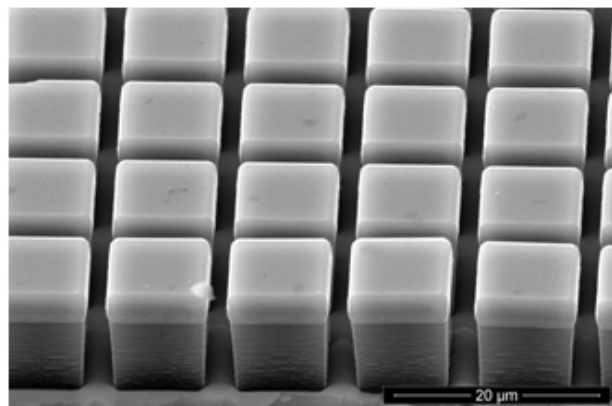


Figure 1. Perspective view SEM micrograph of 3 μm tall Ge microcrystals grown on Si substrate with 8 μm tall and 9 μm wide pillars, spaced by 3 μm gaps.

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PREPARATION AND CHARACTERIZATION OF IRON (III) OXIDE NANOCOMPOSITES SUBSTITUTED WITH SCANDIUM

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This work describes a preparation and characterization of nanoparticles of iron(III) oxide substituted with scandium embedded in silica matrix. The nanoparticles were prepared by the conventional sol-gel method yielding mostly $\text{-Fe}_2\text{O}_3$ substituted with various amount of scandium(III) ions.

Mossbauer spectroscopy was carried out to determine the content of other iron oxides phases. System was characterized by magnetic measurements. Powder X-ray diffraction was used to verify the composition and to determine the lattice parameter and particle size.

$\text{-Fe}_2\text{O}_3$ is formed at the temperatures of 1000 and 1100 °C at composition $\text{Fe}_{2-x}\text{Sc}_x\text{O}_3$ for $x = 0.2$ and at temperature 1100 °C for $x = 0.1$. After annealing at 900 °C, $\text{-Fe}_2\text{O}_3$ is formed in the samples with $x = 0.6$. At temperatures higher than 1250 °C, $\text{-Fe}_2\text{O}_3$ is transformed into hematite. This

temperature is significantly higher than temperatures given in literature (600-700 °C) [1],[2].

Lattice parameter of $\text{-Fe}_2\text{O}_3$ is linearly dependent on the scandium content and depends also on the annealing temperature. Particles size increases with increasing annealing temperature. Low temperature Mossbauer spectroscopy shows a dependence of the blocking temperature on the scandium concentration due to weakening of the exchange interactions by the substitution of iron by diamagnetic scandium ions.

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Preparation of oriented Co_3O_4 films by decomposition of Na_xCoO_2

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Materials based on cobalt oxides have attracted great interest in the production of electronic thin films, heterogeneous catalysts, and gas sensors. In this work we studied the formation and structural characterization of highly (111) - oriented Co_3O_4 (cubic spinel structure) films prepared by novel procedure from (001) - oriented layered sodium cobaltate Na_xCoO_2 . The Na_xCoO_2 films exhibits self-texture growth with crystallographic c-axes perpendicular to the film plane independently of substrate used for deposition.

The Na_xCoO_2 films with different content of sodium were deposited on single crystal and ceramics substrates by chemical solution deposition (CSD) and crystalized by annealing at temperature of 700 °C. Subsequently, the (111) -

oriented Co_3O_4 films were obtained during post- growth annealing at the temperature of 900 °C. Films were mainly characterized by X-ray diffraction, scanning electron microscopy (SEM), and atomic force microscopy (AFM).

The Co_3O_4 grows (pseudo)epitaxially with the epitaxial relation Co_3O_4 (111)[-121] // $\text{-Al}_2\text{O}_3$ (0001)[10-10] as determined from scan and pole figure measurements. The degree of preferred orientation observed in Co_3O_4 depends on the content of Na in starting Na_xCoO_2 phase.

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