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Piezoelectric Response of Cadmium Sulfide Nanorod Crystals Grown from Gas Phase by Using Ag and Au Catalyst

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The paper describes macroscopic and AFM measurements of piezoelectric response of a macroscopic array of nanorod crystals of CdS and single nanorod crystal of CdS, respectively. The CdS nanorod crystals grown using Ag catalyst are presented for the first time. It is shown that these crystals have an irregular shape of six-sided polyhedron and demonstrate piezoelectric response similar to their counterpart crystals grown from Au catalyst which have a perfect hexagonal shape and wurtzite structure. The irregular shape of Ag catalyzed CdS nanocrystals is discussed based on the assumption of their sphalerite crystal symmetry.

Keywords: Cadmium sulfide, Nanorod crystal, Catalyst, Piezoelectricity.

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1. INTRODUCTION

Generators of mechanical energy are an important part in the cluster of energy harvesting devices. They are usually designed on the basis of piezoelectric effect [1,2]. This existing approach is developed as independent technology and entity that is designed on the basis of drastically different physical principle and diverse engineering approach as compared to other energy conversion devices to uniquely harvest a particularly type of energy.

We report preparation and investigation of a piezoelectric cell that is designed for harvesting mechanical energy using nanotechnology. Piezoelectric converters of energy based on nanorod crystals of wurtzite symmetry are well known. ZnO, CdS, etc., nanorod crystals of wurtzite symmetry have been reported to demonstrate a piezoelectric response [3-5]. The perfect wurtzite structure of those crystals, in turn, is achieved by using specific catalyst for their growth. As a rule, such a catalyst is gold because it is not oxidized and its small clusters can melt at relatively low temperatures to form a eutectic mixture with the growing semiconductor material.

Here we report the use of Ag catalyst for synthesis of CdS nanorod crystals. We show that despite of irregular shape of these crystals they still demonstrate piezoelectric response similar to their counterpart nanorod crystals grown from Au catalyst which have a perfect hexagonal shape and wurtzite structure.

2. EXPERIMENTAL

2.1 Sample preparations

CdS nanorod crystals were synthesized through thermal co-evaporation of CdS and sulfur powders in four-temperature quasi-closed space equipped with a cryogenic sorption vacuum system. For crystals grown on a substrate covered with Au catalyst seeds, the following temperatures have been used: CdS powder was at 740 ^{0}C, sulfur powder at 140 ^{0}C, substrates at 615 ^{0}C to 460 ^{0}C, and oversaturation time was 10 minutes. The purpose of application of silver catalyst was to get nanorod crystals of small length suitable for piezoresponse force microscopy (PFM) measurements [6,7]. So, substrate temperature was 600 ^{0}C and oversaturation time was 2 minutes.

The substrates used were ITO/glass plates with gold or silver nanocluster array obtained by vacuum evaporation of Au or Ag layer with effective thickness 2-5 nm followed by its annealing.

2.2 Measurements

Piezoelectric measurements of macroscopic samples were performed at room temperature by a contact method to provide an acoustic contact and transfer of ultrasound vibrations to the sample. An acoustic generator G-117, a piezo-transducer based on PZT material, a characteriograph G1-38, a voltmeter Keythley-2000 and an oscillograph TDS Textronix were used for these purposes. Piezoelectric response of the piezo-transducer was measured separately in order to exclude contribution of systematic error to the results.

The PFM measurements have been performed using an MFP-3D AFM system from Asylum Research with an 85 x 85 μm^2 x 15 μm closed loop scanner. Diamond coated, doped DCP-11 AFM probes (NT-MDT) with a nominal spring constant of ~ 6 N/m were used because of their high wear resistance. An F10A voltage amplifier from FLC Electronic was used in order to amplify the excitation voltage provided by the AFM controller. The response signal from the AFM cantilever was processed by an SR 830 DSP lock-in amplifier from Stanford Research Systems and fed back to the AFM controller to create a position dependent PFM map.

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3. RESULTS AND DISCUSSIONS

3.1 CdS nanocrystals grown by using Au catalyst

CdS crystals synthesized by using Au catalyst demonstrated a perfect hexagonal shape which is typical of wurtzite crystallographic structure (Fig.1).

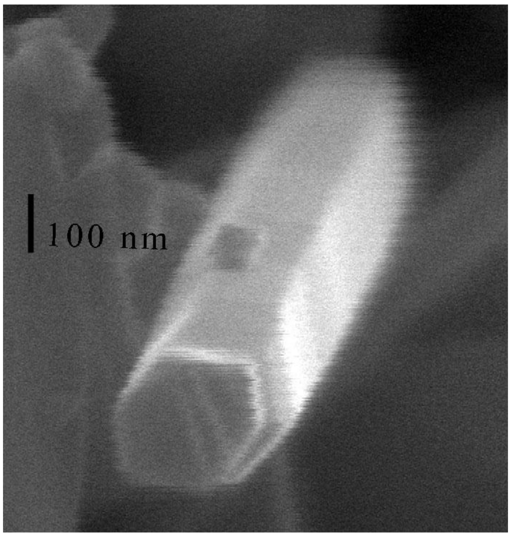

Fig. 1 – Morphology ofa wurtzite CdS nanorod crystal grown with Au catalyst.

Macroscopic measurements showed that an array of nanorod crystals has a piezoelectric response, although the resonance peak is smeared and has a low Q-factor (Fig.2). This may be due to the fact that the length and width of the nanocrystals are not homogeneous and vary in the sample, so the range of eigenfrequencies is scattered.

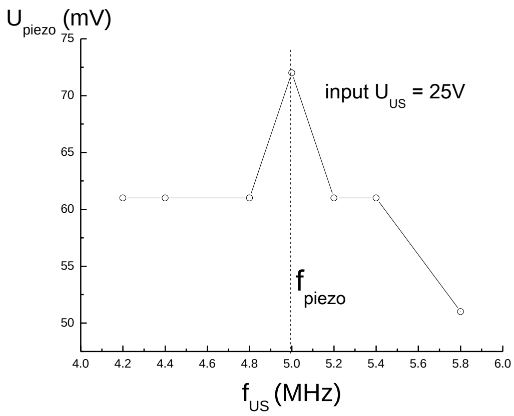

Fig. 2 – Piezoelectric response of a macroscopic CdS nanorod array grown by using an Au catalyst and sandwiched by ITO bottom and Au top electrodes.

The amplitude of the piezoelectric response was found to have a linear dependence on the input voltage of the generator. Based on the ratio of the output and input amplitudes (Fig.2) the energy conversion efficiency of the piezoelectric cells based on CdS nanorod arrays has been roughly evaluated to be in the range of 0.3 to 1.5 %.

3.2 CdS nanocrystals grown by using Ag catalyst

Typical morphology of CdS nanocrystals grown by using Ag catalyst is shown in Fig.3.

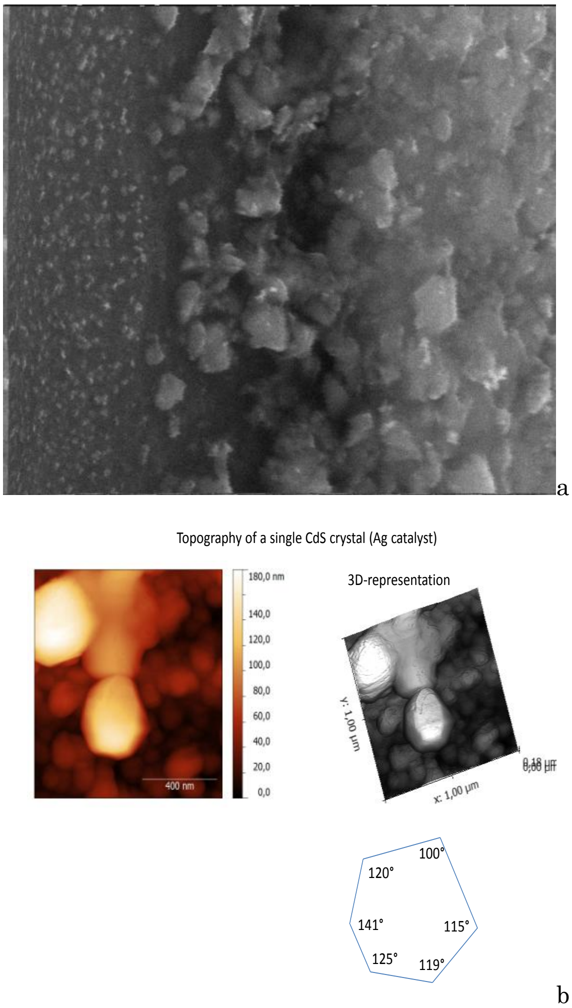

Fig. 3 – (a) SEM and (b) AFM images of morphology of CdS nanocrystals grown with Ag catalyst.

As can be seen, the shape of the crystals represents a six-sided polyhedron (Fig.3 b) with the irregular shape. Such a shape of nanocrystals can be explained by both-wurtzite and sphalerite symmetry of the crystals. For wurtzite symmetry, the reason of this irregularity may be related to the kinetics of crystallization under the small liquid Ag droplet on the surface of substrate which undergoes a non-uniform wetting. A similar irregularity has been observed in our previous study on synthesis of CdS nanocrystals by vapor-solid mechanism [8]. Whereas the *C* axis of the growing wurtzite crystal is directed normally to the substrate, in case of a sphalerite structure the growth direction of the crystal is tilted to the substrate and a six-sided polyhedron can be observed also. But orientation of axis of the piezoelectric response will be tilted to the substrate surface as well.

Piezoelectric response of CdS nanocrystals grown with Ag catalyst is demonstrated in Fig. 4.

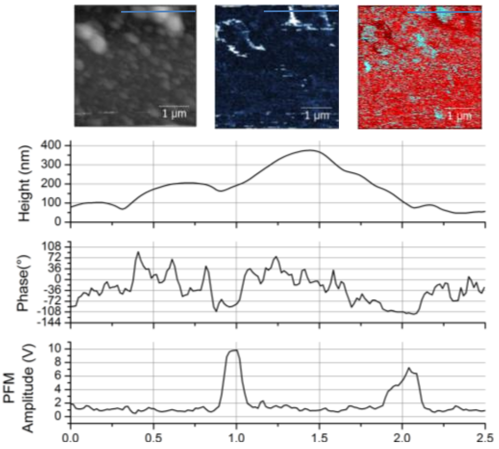

Fig. 4 – Images of morphology, phase and amplitude changes of PFM signal (from the left to the right at the top of the figure) of CdS nanorod array grown with Ag catalyst and corresponding profiles of height, phase and amplitude along the blue line indicated on the images.

It can be seen that the piezoelectric signal demonstrates a clear change of amplitude near the nanorod edges. That means that the signal can be produced due to mechanical deviation of the nanorod crystal in the course of the AFM tip movement. This conclusion is valid in respect to the wurtzite crystallographic structure of the crystals whose C-axis is perpendicular to the substrate surface. However, in case of the tilted sphalerite nanocrystal piezoresponse can be observed from the side faces. Hence, changing of PFM amplitude near the nanorod edges can be explained by angularity of sphalerite nanocrystals as well.

4. CONCLUSIONS

CdS crystals have been synthesized in the form of nanorod arrays using Ag and Au catalyst nucleation seeds and their ability for piezoelectric response has been evaluated. The Au catalyst gives rise to wurtzite crystals of CdS with the perfect hexagon shape, whereas Ag catalyst yields nanorod crystals with the shape of irregular six-sided polyhedron whose symmetry is debatable between wurtzite and sphalerite one. Despite the difference in the shape of the crystals the both types of arrays demonstrate piezoelectric response which can be used for conversion of mechanical energy to electricity. However, additional studies should be undertaken to enhance the efficiency of the above structures.

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