Formation of CdSe nanoclusters in SiO_x thin films

D. Nesheva^{a,*}, H. Hofmeister^b

^a*Institute of Solid State Physics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria*

^b*Max Plank Institute of Microstructure Physics, D-06120, Halle, Germany*

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Abstract

CdSe nanoclusters embedded in silicon oxide layers are produced by sequential physical vapor deposition of SiO_x ($x \approx 1.5$) and CdSe on crystalline silicon substrates at room temperature. High-resolution electron microscopy is used to prove the formation of CdSe nanoclusters as well as to study their shape, size and structure. Cross-sectional electron micrographs of the as-deposited samples reveal clusters with nearly spherical shapes, which are not arranged in a plane. The spatial distribution of the CdSe clusters follows the surface morphology of the SiO_x films. The average size of the nanoclusters is about two times greater than the nominal thickness of the CdSe layers deposited. Upon annealing the samples at 670 K for 80 min, a slight size increase is observed accompanied by some improvement in crystallinity of the CdSe nanoclusters. The σ/a ratio (a : average size of nanocrystals, σ : half-width at half-maximum of size distribution) found for 1-nm CdSe deposited on 20-nm SiO_x is 0.13–0.14, while for 2-nm CdSe deposited on 40-nm SiO_x it is 0.19. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Fabrication of semiconductor nanoparticles is very important for realization of new functional quantum devices [1]. Various techniques, such as epitaxial nanocrystal growth, gas evaporation, co-sputtering, laser ablation, doping in glasses, colloidal methods, crystallization of amorphous materials, have already been applied ([2,3] and references therein) for fabrication of nanoparticles. Among them the Stranski–Krastanow self-organized epitaxial growth of III–V [4] and more recently II–VI semiconductor quantum dots [5,6] in strained systems has attracted much attention. This mechanism takes place on the smooth surface of a crystalline material but it cannot be used for nanocrystal growth on a rough surface. It has been shown [7–10] that, in this case a nonepitaxial self-organized nanocluster formation is possible. It occurs on the rough surface of amorphous thin films deposited by means of physical evaporation, sputtering or glow-discharge techniques. As for the mechanism of the cluster formation, the partial wetting character of Ga with respect to SiO_x was considered [7] as responsible for the formation of liquid Ga nanoclusters on the surface of

SiO_x thin films. On the other hand, Drüsedau et al. [8] assumed that the existing valleys of the thin film a-Si:H surface support clustering of Mo, W, which arrange chains with a length up to several hundreds of nanometers and a thickness much greater than the nominal one of the deposited metal layers. An intentionally created surface roughness on a ZnSe crystalline surface has also been used [9] for obtaining ZnCdSe quantum dots, but the size distribution of those dots was rather wide.

In a previous work [10], we have reported the fabrication of CdSe nanoparticles in a thin film SiO_x matrix by means of a multilayer deposition approach. A size-induced increase in the optical band gap of CdSe nanocrystals and fine structure in their absorption spectra has been observed and related [10,11] to a relatively narrow nanocrystal size distribution. The technique employed for fabrication of those nanocrystals was based on the assumption that during the deposition of ultrathin films of thermally evaporated CdSe on a rough surface of another thin film, nanoclusters might be formed in the surface valleys. In this article, a high-resolution electron microscopy study of the CdSe nanocluster formation and size distribution is reported and a mechanism for this formation suggested. The influence of annealing on the size and structure of CdSe nanoclusters is also investigated.

* Corresponding author.

Fig. 1. Cross-sectional view of the as-deposited “2-nm” sample. CdSe nanoparticles of nearly spherical shape are disposed in a heterogeneous SiO_x -CdSe layer sandwiched between two SiO_x layers. The lower left inset displays the three-layer structure at low magnification. The upper right inset (diffractogram) reflects the crystallinity of the particles.

2. Experimental details

Two types of three-layer structures $\text{SiO}_x(20\text{-nm})/\text{CdSe}(1\text{-nm})/\text{SiO}_x(20\text{-nm})$ (“1-nm” samples) and $\text{SiO}_x(40\text{-nm})/\text{CdSe}(2\text{-nm})/\text{SiO}_x(20\text{-nm})$ (“2-nm” samples) were deposited on polished silicon substrates, maintained at room temperature during the deposition procedure. Thermal evaporation of powdered CdSe (Merck, “suprapure”) and granular SiO from two independent tantalum crucibles was carried out at a vacuum of $\sim 10^{-3}$ Pa. The film thickness and deposition rate of both materials were controlled during deposition by two preliminary calibrated quartz monitors MIKI-FFV, whose quartz crystal heads were fixed above the respective source. In order to ensure the same composition of the SiO_x matrix ($x \approx 1.5$ [10]) in all samples, the deposition rate of SiO_x was kept constant (~ 3.5 nm/s). The SiO_x films were produced in a one-step procedure while the CdSe ones were deposited in a step-by-step manner. CdSe with a nominal thickness of 1 or 2 nm was deposited (at a nominal rate of 5 nm/s) as the substrates were rotated at a rate of 30 and 20 turns/min, respectively. The rotating substrates spent only 1/12 part of the turn time over the CdSe source and, thus, 10–20 CdSe ‘sublayers’, with a nominal thickness of ~ 0.1 nm in each step, form the CdSe layers of both kinds of structures. Some as-prepared films were annealed in air at 670 K for 80 min. The X-ray diffraction studies performed have shown [10] that CdSe nanocrystals of hexagonal wurtzite structure were formed after annealing.

High-resolution electron microscopy (HREM) measure-

Fig. 2. Cross-sectional view of the “2-nm” sample upon annealing in air at 670 K for 80 min. The low magnification representation and the diffractogram point to CdSe nanoparticles of increased size and improved crystallinity with respect to the as-deposited sample.

ments were performed by means of a JEM 4000 EX operating at 400 kV. Electron micrographs were recorded at 110 000 and 500 000 times magnification using optimum contrast conditions (near Scherzer defocus).

3. Results

The results obtained on the as-deposited “2-nm” three-layer structure are shown in Fig. 1. The low magnification inset (lower left) illustrates that CdSe does not form a continuous layer. Instead, nearly spherical CdSe nanoparticles, partly isolated and partly in contact with each other, are disposed in a heterogeneous SiO_x -CdSe layer of up to 10-nm thickness. The average size of CdSe nanoparticles and the thickness of the heterogeneous SiO_x -CdSe layer are significantly greater than the nominal CdSe layer thickness. Fig. 2 illustrates the changes upon annealing of the “2-nm” samples at 670 K for 80 min. While the crystal lattice of the particles remains oriented randomly, their sizes increase a little and the spherical appearance is improved. From the high-resolution imaging of lattice plane fringes and by comparison of the diffractograms (circular inset in the upper right) of both images, it is obvious that the crystallinity of the CdSe nanoparticles is improved upon annealing.

The size distribution of CdSe nanoparticles in as-deposited and annealed “1-nm” and “2-nm” samples is shown in Fig. 3a and b, respectively. It is seen that in as-deposited structures the maximum of the distribution corresponds to average nanocluster sizes, which are more than two times greater than the respective nominal CdSe layer thickness.

Fig. 3. Size distribution of self-organized CdSe nanoparticles in as-deposited and annealed: (a) SiO_x(20-nm)/CdSe(1-nm)/SiO_x(20-nm) and (b) SiO_x(40-nm)/CdSe(2-nm)/SiO_x(20-nm) structures. An increase in the mean particle size and width of size distribution is seen in both “1-nm” and “2-nm” samples.

After annealing a well-expressed increase in the average nanocrystallite diameter is observed in both structures, accompanied by a slight increase in the width of size distribution. Making Gaussian fits of the results shown in Fig. 3a and b, values of ~ 0.13 and 0.14 have been obtained for the σ/a ratio in as-deposited and annealed “1-nm” structures, respectively (here σ is half-width at half-maximum of the size distribution and a the average nanocrystallite diameter). In both as-deposited and annealed SiO_x(40-nm)/CdSe(2-nm)/SiO_x(20-nm) structures $\sigma/a \approx 0.19$. This nanocrystal size-distribution is slightly narrower than those reported for CdS [12] and Ge [13] nanocrystals, which were grown in thin SiO₂ matrix during the annealing of thin amorphous films of CdS-doped silica and Si_{1-x}O_xGe_y, respectively.

4. Discussion

At the first stage of thin film deposition, the formation of embryos depends on the temperature, chemical nature, structure and cleanness of the substrate surface [14]. In particular, the presence of steps or other defects on the substrate surface induces an increase in the embryo concentration. On the other hand, it is known [14] that during the nonepitaxial growth of thin films the top surface of these films is rough and the roughness amplitude varies with the deposition techniques. In the case of thermal evaporation of materials this amplitude is proportional to the square root of the film thickness d [14]. Furthermore, in a recent study [15], it has been shown that curvature and stress at a rough or even disordered surface strongly affect reaction rates at a solid interface as they create different environments at different reaction sites.

The technique we developed [10] for fabrication of CdSe nanocrystals was based on the assumption that during the deposition of ultrathin films of thermally evaporated CdSe

on a rough surface, these films will be discontinuous and, probably, nanoclusters might be formed in the surface valleys. In this approach it has been taken into account that the thicker the thermally evaporated layer, the greater its surface roughness; and in all samples the SiO_x thickness d_{SiO} was 20 times greater than the CdSe one d_{CdSe} . The HREM micrographs presented in Figs. 1 and 2 show that, in fact, a real self-organized CdSe nanocluster formation takes place on the rough surface of SiO_x. However, the great thickness of the heterogeneous SiO_x-CdSe layer indicates that nanoclusters should not be formed only in the surface valleys. Most likely, the spatial distribution of the CdSe clusters follows the surface morphology of the SiO_x films. We assume that, at the very beginning of CdSe film deposition, embryos are formed at those positions on the SiO_x surface at which the curvature and lattice stress are the greatest. Further CdSe deposition does not create new embryos but leads only to an increase in the nanocluster size. This assumption is supported by the relatively narrow nanocluster size distribution observed (Fig. 3a and b). As the positions with large surface curvature and lattice stress are disposed accidentally, some embryos are created rather close to each other and, even at the first stage of nanocluster growth, coalescence of some nanoclusters may occur. Figs. 1 and 2 show that, by using a procedure of step-by-step CdSe deposition at low substrate temperature and deposition rate, the thickness ratio of $d_{\text{SiO}}/d_{\text{CdSe}} = 20$ ensures such a SiO_x surface roughness that the CdSe nanocluster growth is interrupted at the first stage of coalescence.

5. Conclusions

The self-organized formation of CdSe nanoclusters during physical vapor deposition of CdSe on a rough surface of amorphous SiO_x has been proved by high-resolution

electron microscopy studies. A relatively narrow cluster size distribution has been established. It confirms our previous assumption concerning this distribution, which has been made [10,11] on the basis of the results from optical absorption measurements. The suggested mechanism of cluster formation implies that this approach may be applied to the fabrication of nanoclusters from other II–VI compounds (CdS, ZnSe, etc.), embedded in the thin film amorphous matrix.

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