Composition and structure of Zn$_{x}$Cd$_{1-x}$Se single layers prepared by thermal evaporation of ZnSe and CdSe

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Abstract. Single layers of Zn$_{x}$Cd$_{1-x}$Se with five different compositions and thickness of 400 nm have been prepared by thermal vacuum evaporation, through alloying of ultra thin ZnSe and CdSe films with equivalent thickness of 0.12, 0.25 or 0.37 nm. The deposition was carried out on rotating substrates kept at room temperature. The layer composition was varied by alloying ZnSe and CdSe films with different equivalent thicknesses. The film composition $x = 0.39, 0.52, 0.59, 0.69$ and $0.8$ has been determined by Energy-Dispersive Spectroscopy and confirmed with Raman scattering data. The microstructure of Zn$_{x}$Cd$_{1-x}$Se has been investigated by Atomic Force Microscopy and Raman scattering measurement. The Atomic Force Microscopy results have revealed that the layers are nanocrystalline and the grain size is $\leq 20$ nm. The Raman scattering data have shown four replicas of the longitudinal optical phonons, thus confirming the conclusion for the layer crystallinity. The obtained results have shown that the applied deposition technique makes possible preparation of ternary nanocrystalline Zn$_{x}$Cd$_{1-x}$Se layers with desired compositions.

1. Introduction

Ternary alloys of ZnCdSe are an important class of semiconductors which are applicable in fabrication of optoelectronic devices operating in the entire visible spectrum, as well as in fabrication of solar cells, thin film transistors, etc. [1]. The routes for preparation of ternary II-VI semiconductor layers are based mainly on application of molecular beam epitaxy [2,3] and electrodeposition [4,5] techniques. Ternary alloys of II-VI semiconductors (ZnCdSe, ZnSSe) included in zinc-selenide based quantum structures have demonstrated considerable promise as short-wavelength light sources, fast switching devices, etc. [6-8]. The interest in inclusion of such alloys in low-dimensional structures is high [3,9-12] since they offer possibilities to change their lattice constant and optical properties by changing the composition and this gives them advantages over binary compounds (ZnSe, CdS). For preparation of multilayers (MLs) with good stability and periodicity or production of nanocrystals in the quantum structures with narrow size distribution, molecular beam epitaxy (MBE) or metal-organic chemical vapour deposition (MOCVD) are normally applied. However, both techniques are quite expensive and, in addition, MOCVD normally uses dangerous gases. Besides, high quality crystalline ZnSe or
GaAs substrates are required for the epitaxial growth. This has motivated a considerable research activity in the field of preparation of low-dimensional structures by non-epitaxial film growth and application of less expensive vapour deposition techniques [13 and References therein] and electrodeposition [4].

In several previous papers [13,14,15] we have reported on preparation of amorphous/nanocrystalline multilayers with good artificial periodicity and smooth interfaces nanostructured thin films by thermal evaporation in vacuum. In this study, a technique for preparation of microcrystalline \( \text{Zn}_x\text{Cd}_{1-x}\text{Se} \) single layers with controlled composition is developed, based on thermal vacuum evaporation. It can be successfully applied for production of \( \text{ZnSe/Zn}_x\text{Cd}_{1-x}\text{Se} \) MLs. Energy-Dispersive Spectroscopy (EDS), Atomic Force Microscopy (AFM) and Raman scattering measurements are carried out to determine the composition and to explore the film microstructure.

2. Experimental

2.1 Sample preparation

Thermal evaporation of \( \text{ZnSe} \) and \( \text{CdSe} \) powders (Merk, Suprapure) from two independent, simultaneously heated tantalum crucibles was applied for the preparation of \( \text{Zn}_x\text{Cd}_{1-x}\text{Se} \) layers with five different compositions and thickness of 400 nm. The crucibles were disposed in the bottom of two cylindrical screens (not intentionally heated) whose top is close to the substrates. Thus, the deposition of each material was carried out in a quasi-closed volume.

The layers of \( \text{Zn}_x\text{Cd}_{1-x}\text{Se} \) were deposited on crystalline c-Si substrates (Wacker, p-type, 11 \( \Omega/cm \)) kept at room temperature. The native oxide on the c-Si substrates was not removed. During the film deposition the substrates were rotated at a rate \( \nu_r = 20 \) turns/min and during each turn pass they spent over each crucible 1/12 of the turn time. The time \( \Delta t \) between the consecutive deposition of \( \text{CdSe} \) and \( \text{ZnSe} \) is 5/12 of the turn time. The substrate rotation was started after fixing the desired deposition rates for both \( \text{CdSe} \) and \( \text{ZnSe} \). The rates were controlled by two independent preliminary calibrated quartz microbalance systems MIKI FFV. The layer composition was varied by changing the ratio of the deposition rates of both materials; five ratios \( V_{\text{CdSe}}/(\text{nm/s})/V_{\text{ZnSe}}^{\text{nm/s}} \) were used (0.5/1.5, 1.0/1.5, 1.5/1.5, 1.5/1.0, 1.5/0.5). Thus, five kinds of \( \text{Zn}_x\text{Cd}_{1-x}\text{Se} \) single layers were prepared by alloying of the consecutively deposited small portions of \( \text{CdSe} \) and \( \text{ZnSe} \) with equivalent layer thicknesses \( d_e = 0.12 \) nm (at 0.5 nm/s), 0.25 nm (at 1.0 nm/s), 0.37 nm (at 15 nm/s).

It has been shown [16] that \( \text{CdSe} \) single layers prepared at the same deposition conditions (i.e. application of cylindrical screens, same distance between the crucible and the substrates, similar deposition rates and rates of substrate rotation) are stoichiometric. Based on this and keeping in mind the ratio of the deposition rates measured, the following compositions were expected: \( x_e \approx 0.25 \) (\( V_{\text{CdSe}}^{\text{nm/s}}/V_{\text{ZnSe}}^{\text{nm/s}} = 15 \) nm s\(^{-1}\)/5 nm s\(^{-1}\)), \( x_e \approx 0.4 \) (15/10), \( x_e \approx 0.5 \) (15/15), \( x_e \approx 0.6 \) (10/15), \( x_e \approx 0.75 \) (5/15).

2.2 Sample characterization

The layer thickness was determined by optical transmission measurements [17] which showed that the deviation of the film thickness from the expected one did not overcome 5%. The sample composition was determined by EDS measurements using a JEOL Scanning Electron Microscope (JSM-6390) operating at an accelerating voltage of 25.00 kV. The samples were uncoated; the element used for optimization was Iron. At least two different points on the sample surface were explored.

The surface morphology of the layers was investigated by AFM measurements that were carried out using a Multimode V (Veeco, Santa Barbara, CA). Imaging was performed in tapping mode and height, amplitude, and phase images were recorded. The scan rate was in the range 1-2 Hz, the images resolution was 512 lines per scan direction. At least three different points on the sample surface were explored. Silicon cantilevers with a super sharp spike tip (TESP-SS, Veeco-probes)\(,d\) a nominal resonance frequency of 320 kHz and a typical force constant of 42 N/m were used. The tip radius for these probes is in the range 2-5 nm. Image processing was performed by means of the Nanoscope 7.30 programme. All the images were flattened and no further processing was carried out.
Raman scattering measurements of Zn$_x$Cd$_{1-x}$Se single layers were performed in the backscattering geometry, by Jobin-Yvon T64000 triple spectrometer system, equipped with a confocal microscope and a nitrogen-cooled CCD detector. All spectra were collected by using 514.5 nm (2.41 eV) line of mixed Ar$^+/\text{Kr}^+$ ion laser at room temperature in the air. A low output laser power ($\leq 5$ mW) was used to avoid local heating and subsequent Zn$_x$Cd$_{1-x}$Se layer decomposition.

3. Results and Discussion

Table 1 presents the average Zn, Cd and Se atomic percentages determined from the EDS data with a maximum error of 5%. It is seen from the table that some films have a slight Se-enrichment; the maximum Se/metal ratio obtained for these films is 1.27. It is smaller than the Se/Zn value (1.42) reported in Ref 18 for 260 nm thick ZnSe layers prepared by thermal vacuum evaporation at room substrate temperature. The lower Se-enrichment of our Zn$_x$Cd$_{1-x}$Se layers can be related to the fact that both ZnSe and CdSe were deposited in a quasi-closed volume.

Table 1. Average EDS data for the chemical composition of the prepared Zn$_x$Cd$_{1-x}$Se thin films.

| $V_d^{\text{CdSe}}/V_d^{\text{ZnSe}}$ | Zn (at.%) | Cd (at.%) | Se (at.%) | $x_e$ | $x_m$ | $x_m-x_e$ |
|---|---|---|---|---|---|---|
| 1 | 3 | 19.6 | 30.5 | 49.9 | 0.25 | 0.39 | 0.14 |
| 2 | 1.5 | 23 | 20.9 | 56.1 | 0.4 | 0.52 | 0.12 |
| 3 | 1.0 | 25.8 | 18 | 56.2 | 0.5 | 0.59 | 0.09 |
| 4 | 0.667 | 32.8 | 15 | 52.2 | 0.6 | 0.69 | 0.09 |
| 5 | 0.333 | 34.4 | 8.4 | 57.2 | 0.75 | 0.80 | 0.05 |

According to the model applied to ternary A$_x$B$_{1-x}$C alloys, in particular to Zn$_x$Cd$_{1-x}$Se [2,9], two sublattices exist in such alloys: one consisting solely of Se atoms and the other one consisting of Zn and Cd atoms in a random arrangement. The experimental $x_m$-values given in Table 1 have been obtained assuming that in the metal sublattice no Se atoms are included and, in accordance with the Zn$_x$Cd$_{1-x}$Se formula, the sum of the metal atom percentages has been considered as 100 % of metal atoms. Thus obtained $x_m$-values indicate that layers of five different compositions were successfully produced. One can see from figure 1 that the experimental points lie on a line $x_m = A + Bx_e$ ($A = 0.19 \pm 0.02$, $B = 0.82 \pm 0.04$) which indicate that a linear relation exists between the expected and experimental compositions. Using this relation, it is possible to produce films with desired compositions by means of the above described deposition approach. Further studies will define the range of $x$-values for which this linear relation is preserved.

![Figure 1](image1.png)

**Figure 1.** Relation between the expected $x_e$ and EDS determined $x_m$ composition of Zn$_x$Cd$_{1-x}$Se thin films, prepared by thermal evaporation of ZnSe and CdSe in vacuum. The solid line represents a linear fit of the experimental points. Inset: Deviation of the measured layer composition from the expected one versus the ratio of the deposition rates of CdSe and ZnSe. The line is guide to the eye.
The observation that the $B$-value is $<1$ means that there exists a systematic deviation of the experimental composition from that expected; for all compositions the Cd inclusion is less than that expected on the basis of the ratio of the deposition rates. One can see from Table 1 and the inset in figure 1 that the Cd-deficiency increases with increasing ZnSe deposition rate and decreasing the ratio of the deposition rates. An enhanced redesorption of the Cd deposit has been reported [19] during overgrowth of CdSe layers by ZnSe which has been related to Cd segregation and replacement of Cd by Zn in the topmost surface. A similar process may be responsible for the observed deviation of the experimental composition from that expected. Besides, this process causes [19] a strong intermixing of the ZnSe and CdSe layers, which is in favour of the preparation technique described here, since the process will facilitate fabrication of layers with a quite homogeneous composition at the nanoscale.

AFM surface image and grain size distribution of a 400 nm thick Zn$_x$Cd$_{1-x}$Se single layer with $x = 0.59$ are depicted in figure 2 (a) and (b), respectively. The surface images of the layers with the other compositions are very similar. They reveal that the layers are nanocrystalline with an apparent grain size of ~ 23 nm. Normally the apparent AFM size depends on the tip size; the smaller the tip size, the closer the apparent grain size to the real one. In our experiments the tip apex size was 8 nm and hence one can assume that the average grain size is around or less than 20 nm. The AFM experiment has also revealed a tendency for the Zn$_x$Cd$_{1-x}$Se layer hardness to increase with increasing Zn content.

Micro-Raman spectra of five layers with different compositions, which were taken under excitation with the 514.5 nm laser line, are shown in figure 3. The longitudinal optical (LO) phonons demonstrate a single phonon behaviour, expected for Zn$_x$Cd$_{1-x}$Se [2,3]. A series of 4 LO Raman peaks (at ~ 240, ~ 480, ~ 720, ~ 960 cm$^{-1}$) is observed in the spectra of all samples. This series originates from so-called LO-phonon replicas, well known in polar crystalline semiconductors [18]. The appearance of four LO peaks in all spectra is an indication that the films are crystalline rather than amorphous and this observation is in agreement with the AFM results. The FWHM of the 1LO bands is quite large (~ 17 cm$^{-1}$) which could be due to both imperfect film crystallinity and some variations in the film composition at the nanoscale. According to the structural model of Zn$_x$Cd$_{1-x}$Se [2,9], Zn and Cd atoms in the metal sublattice are randomly arranged and no short-range order is imposed. However, experimental studies of ZnSe/ZnCdSe/ZnSe structures, produced by submonolayer insertion of Cd into ZnSe matrices, have shown that the resulting distribution of Cd along the growth plane is strongly inhomogeneous in many cases. Formation of nanosized Cd-rich regions has been observed in Zn$_x$Cd$_{1-x}$Se grown by different MBE systems [20-23]. It is considered that the formation of those Cd-enriched islands is caused by a strong mismatch of the lattice constants of ZnSe and CdSe, resulting in an increase of the diffusion length of Cd [20,23]. Hence, one can think that the relatively large FWHM
of the Raman band is due to existence of Cd-rich regions in our layers.

The 1LO Raman bands in the Raman scattering spectra of all samples are disposed between the 1LO bands of stoichiometric ZnSe (252 cm\(^{-1}\)) and CdSe (210 cm\(^{-1}\)) (Figure 4). As expected, a gradual red-shift is seen with increasing Cd content, which confirms that Zn\(_x\)Cd\(_{1-x}\)Se thin films of various compositions have been successfully prepared by the applied deposition technique. Figure 5 compares the observed 1LO position changes with experimental results reported for Zn\(_x\)Cd\(_{1-x}\)Se films produced by MBE [2] and a theoretical curve [9]. One can see that the 1LO positions we determined are close to both experimental and theoretical curves. This coincidence gives compositions which are close to those determined by EDS and indicates that the internal stress in these films is not excessively high.

**Figure 3.** Micro-Raman spectra of five Zn\(_x\)Cd\(_{1-x}\)Se layers measured under excitation with the 514.5 nm line of an Ar\(^+\)/Kr\(^+\) laser. All spectra correspond to the same scale but offset for clarity.

**Figure 4.** Shift of the 1LO in the Raman spectra of five Zn\(_x\)Cd\(_{1-x}\)Se layers measured under excitation with the 514.5 nm line of an Ar\(^+\)/Kr\(^+\) laser. All spectra correspond to the same scale but offset for clarity.

**Figure 5.** Comparison of the composition-induced shift of the 1LO band obtained in this study (stars) with experimental [2] and theoretical [9] data reported by other authors for Zn\(_x\)Cd\(_{1-x}\)Se layers.

### 4. Conclusions

Single layers from Zn\(_x\)Cd\(_{1-x}\)Se with five different compositions have been prepared by parallel thermal evaporation of ZnSe and CdSe in vacuum and substrate rotation. Alternating ZnSe and CdSe (island type) films have been deposited on the substrates at room temperature having equivalent thicknesses of 0.12, 0.25, 0.37 nm. Both materials alloy and thus form ternary Zn\(_x\)Cd\(_{1-x}\)Se layer. The EDS investigations performed have given values of \(x = 0.39, 0.52, 0.59, 0.69\) and 0.8, while values of \(x = 0.25, 0.40, 0.50, 0.60\) and 0.75, respectively, were expected from the deposition conditions applied. The observed discrepancy has been related to Cd redesorption during deposition of ZnSe on CdSe surface.
The microstructure of the Zn\textsubscript{x}Cd\textsubscript{1-x}Se layers prepared has been explored by AFM and Raman scattering measurements. The AFM results have shown that the layers are nanocrystalline with a grain size $\leq 20$ nm. The Raman scattering results have confirmed the film composition obtained from the EDS data thus proving that the film composition can be successfully varied with varying the deposition conditions. They indicate that the internal stress in the Zn\textsubscript{x}Cd\textsubscript{1-x}Se layers is not very high. The results obtained have proven that this deposition technique allows preparation of ternary Zn\textsubscript{x}Cd\textsubscript{1-x}Se layers with controlled compositions.

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