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Study of Substrate Diffusion in Epitaxial n-Type CdSe Films Grown on GaAs (001) by Pulsed-Laser Ablation

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STUDY OF SUBSTRATE DIFFUSION IN EPITAXIAL N-TYPE CdSe FILMS GROWN ON GaAs (001) BY PULSED LASER ABLATION

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ABSTRACT

N-type CdSe films with thicknesses of 470–630 nm were grown on (001) and 2°-miscut GaAs wafers by ArF (193 nm) pulsed laser ablation of stoichiometric CdSe targets at platen temperatures (T_p) of 250–425°C in vacuum and ambient Ar gas. Film-substrate interdiffusion was studied with Auger depth profiling, as well as energy dispersive x-ray fluorescent spectroscopy (EDS). Both techniques showed that extensive interdiffusion took place at the film-substrate interface for CdSe films grown at $T_p \geq$ 355°C but was greatly reduced at T_p=250°C. Tilting the substrate to be approximately parallel to the ablation plume as well as decreasing the ambient gas pressure also reduced film-substrate interdiffusion.

INTRODUCTION

CdSe with a band gap of 1.7 eV (λ_g=729 nm) and a free exciton binding energy of 14 meV [1] at room temperature has potential for opto-electronic devices operating in the red to near IR spectral range. N-type cubic CdSe also is of interest for heterostructures with p-ZnTe since these two compounds have a lattice constant mismatch of less than 1% (a_{ZnTe}=6.1Å, a_{CdSe}=6.052 Å). However, CdSe or other compound semiconductor films for such applications must satisfy a number of requirements, including (i) epitaxial growth; (ii) high dopability; (iii) near-ideal film stoichiometry; and (iv) freedom from contaminants except for dopants.

Epitaxial CdSe films have been grown on GaAs (001) and on ZnSe/GaAs(001) by molecular beam epitaxy (MBE) [2,3] and metalorganic MBE [4]. Recently, films of epitaxial CdSe, as well as other compound semiconductors [5], were also grown on (001) GaAs by pulsed laser deposition (PLD) [6]. Despite these demonstrations of epitaxial growth, the optimum growth conditions to obtain high quality films require more study, primarily because of the large (7.1%) lattice mismatch between GaAs (a = 5.653Å) and CdSe.

Impurities can be introduced into a film from the deposition chamber atmosphere as well as by substrate diffusion during film growth. Although environmental impurities are reasonably controllable when a low-pressure gas is used for dopants incorporation during PLD [5,7], the diffusion of substrate atoms into the film often takes place in the temperature range used for epitaxial growth, regardless of the growth technique [8,9]. Film-substrate interdiffusion is difficult to control in many cases, especially for lattice-mismatched heteroepitaxial systems, and becomes more important as the thickness of the layers in semiconductor quantum structures decreases. For instance, interdiffusion can affect the electron and phonon states at the interface and may change the electrical and optical properties of compound semiconductor epilayers. Film stoichiometry is crucial to control the electronic properties of films used in devices since a point defect (vacancy, interstitial) concentration of only 1 part in 10^4 can prevent electrical activation of dopants [5].

This paper deals with film-substrate interdiffusion for epitaxial CdSe films deposited onto GaAs (001) by PLD. The studies were conducted with Auger electron spectroscopy (AES) and energy dispersive x-ray spectroscopy (EDS).

EXPERIMENTAL PROCEDURES

The film deposition set-up is schematically described in Fig. 1. An ArF (3–5 Hz, 193 nm) excimer laser was used for PLD of CdSe films in an ultra high vacuum (UHV) chamber (base pressure ≤ 10^{-9} torr). 6N purity Ar gas was introduced into the chamber through a mass-flow control manifold and the ambient gas pressure was controlled from zero to 50 mtorr using a

throttling valve and pressure-feed back controller. A commercial hot pressed CdSe disk (5N pure) of 1 inch diameter and Cr-doped epi-ready GaAs wafers (semi-insulating) were used as the ablation target and substrates, respectively. The substrates either were attached to the platen with indium, or else silver paint was used to avoid unintentional indium doping. Indium was found in films deposited at $T_P \geq$ 355°C, but little or no indium was detected in films deposited at T_P=250°C, and no silver was found in any film [10].

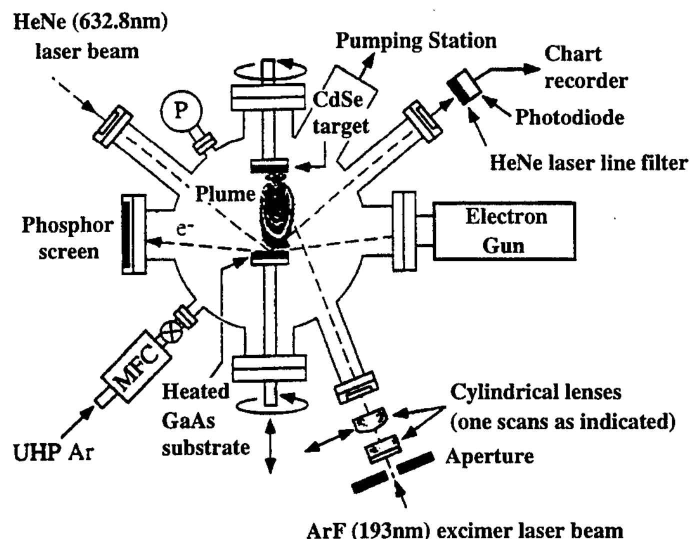

Figure 1. Schematic diagram of the pulsed laser ablation film-growth system

The distance between the target and the substrate was 10 cm. Prior to film growth, oxides on the GaAs substrate surface were eliminated by directing an atomic hydrogen beam (produced by thermally cracking 6N purity H_2 gas) onto the GaAs surface while it was held at 300°C. This treatment was continued until a streaky RHEED pattern characteristic of crystalline GaAs was obtained. The film growth parameters are listed in Table 1. In order to investigate a possible effect on film quality or atomic diffusion due to the momentum transfer from energetic ablated ions/atoms, films were grown with the substrate surface oriented either parallel or perpendicular to the ablation plume axis. Collisions with ambient Ar gas molecules also were used to control the kinetic energy of incident species. The platen on which substrates were mounted was rotated continuously during deposition to obtain uniform-thickness films. X-ray diffraction was performed in the range of $10^\circ \leq 2\theta \leq 70^\circ$ to investigate the films epitaxy.

Table 1. Sample preparation parameters

Sample #	P[Ar] (mtorr)	Bonding Agent	Tilt (*a*) (deg)	T_P (°C)	Substrate Miscut (°)	Film thickness (nm)
CS1 (with In wire)	50	Indium	0	355	2	630
CS2	50	Indium	0	355	2	630
CS3	50	Indium	90	355	2	470
CS4	0	Indium	0	250	±0.1	580
CS5	30	Indium	0	250	±0.1	580
CS6	30	Indium	90	250	±0.1	580
CS7	50	Indium	90	250	±0.1	580
CS8	50	Indium	90	425	±0.1	470
CS9	30	Ag paint	90	250	±0.1	580
CS10	30	Ag paint	0	250	±0.1	580
CS11	50	Ag paint	0	425	±0.1	580

(*a*) Tilt of 0° (90°) corresponds to the ablation plume axis being perpendicular (parallel) to the substrate.

A Perkin Elmer Model 660 Scanning Auger Multiprobe combined with an ion sputter gun was used for the diffusion and interdiffusion studies. AES depth profiling was conducted to obtain elemental profiles as a function of film thickness. In this process the film was removed layer-by-layer and the Auger electrons emitted from fresh surfaces were detected after each sputtering cycle. Ar^+ ions with energy as low as 500 eV was used for the sputtering in order to minimize intermixing within the film and across the film/substrate interface [11]. The ion beam rastering

area was 100 × 100 μm^2 and the analysis area was approximately 0.3 μm in diameter. The sputtering rate was varied from 20 nm/cycle in the film to 1 nm/cycle when approaching the interface, in order to obtain very accurate elemental profiles across the interface. Atomic sensitivity factors that are needed to convert the peak-to-peak heights of the differentiated Auger spectra to atomic concentrations were determined with standard CdSe and GaAs samples. Cd, Se, Ga, and As LMM Auger peaks that do not overlap each other were carefully selected and used for the analysis. Atomic concentrations then were determined at each data acquisition cycle and plotted as a function of distance from the surface of the film.

Energy dispersive x-ray fluorescent spectroscopy (EDS) also was employed to analyze the diffusion of Ga and As into a CdSe film. This new EDS technique has the advantage that diffusion across the interface can be analyzed without destroying the film. Increased spectral intensities due to the reduced travel distances of x-rays originating from the diffused elements were used to estimate the amount of Ga and As out-diffusion. By comparing the integrated intensities of L x-rays for Ga and As in the CdSe film and from bulk GaAs, it could be determined which element had diffused further.

RESULTS AND DISCUSSION

Figure 2 is an example of the x-ray diffraction patterns obtained from CdSe films (sample CS6) prepared in this work. Only (002) and (004) peaks were found in the 10° ≤ 2θ ≤70° range, corresponding to a CdSe epilayer that has a cubic zinc blend structure and (001) orientation [2]. The lattice parameter determined from the diffraction pattern is ~ 6.09 Å, which is very similar to the values obtained in other work [2–4]. Most of the CdSe films prepared in this work exhibited diffraction patterns similar to the one shown in Fig. 2. However, in a few samples, very low intensity hexagonal reflections also were observed in the diffraction pattern [6].

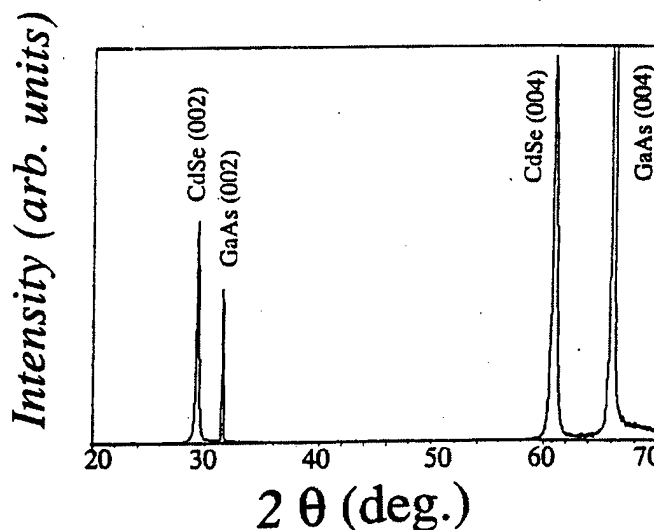

Figure 2. Cu Kα (λ=1.542 Å) X-ray diffraction pattern of CdSe/GaAs film-growth system

AES depth profiling at the film-substrate interface

Figure 3 compares the interfacial composition profiles of sample CS2, grown at 355°C in 50 mtorr of Ar gas without tilting the sample, with the profiles for samples CS3 and CS8, grown at 355°C and 425°C, respectively, in 50 mtorr of Ar with the substrate tilted by 90° (parallel to the ablation plume axis). The effect of the substrate tilt angle alone at a constant Ar pressure of 50 mtorr is shown in Figs. 3 (a) and 3(b). At T_p = 355°C the interface width was reduced by ~44% (from ~180 nm to ~100 nm) as the tilting angle was changed from 0 (normal to the ablation plume) to 90° (approximately parallel to the ablation plume). Comparing Figs. 3(b) and 3(c), an appreciable increase in the interdiffusion occurred when the platen temperature was increased from 355°C to 425°C. The dashed vertical lines in Figs. 3 and 4 are guide to the eye and indicate the approximate boundaries of the interdiffused regions. Figure 4 shows the interfacial composition profile of (a) sample CS2 grown at 355°C in 50 mtorr of Ar gas, and the profiles for samples (b) CS4 and (c) CS7, grown at 250°C in vacuum and in 50 mtorr of Ar gas, respectively. Films CS2 and CS4 were grown with the ablation plume at near-normal incidence on the substrate surface, while sample CS7 was oriented approximately parallel to the axis of the ablation plume.

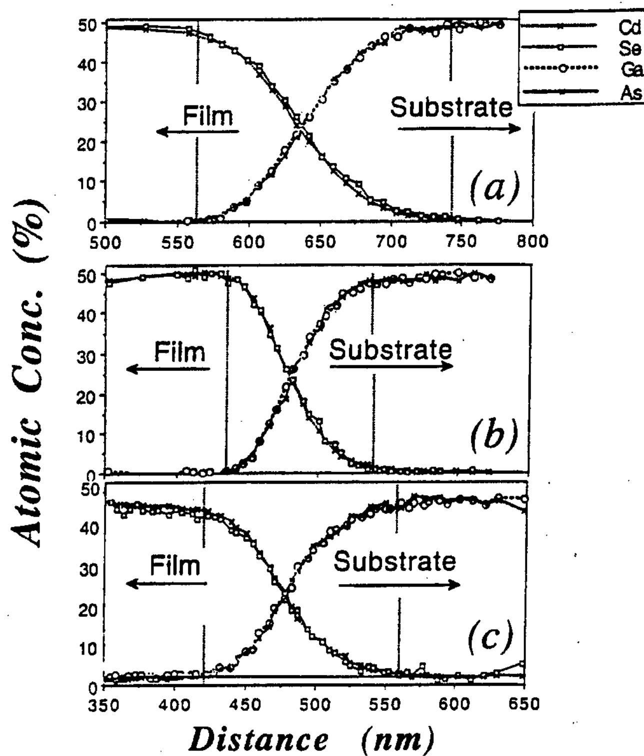

Figure 3. The interfacial composition profiles of samples (a) CS2, grown at 355°C in 50 mtorr of Ar gas without tilting the substrate, and (b) CS3 and (c) CS8, grown at 355°C and 425°C, respectively, in 50 mtorr of Ar gas with the substrate tilted 90°.

The much larger interface width in Fig. 4(a) is clearly due to the higher substrate temperature. Tilting the substrate as well as changing the ambient gas pressure from 0 to 50 mtorr also reduced the interface width by ~ 50%, as shown in Figs 4(b) and (c). The smaller but still clear difference in interfacial widths (~40 nm vs. ~20 nm) in Fig. 4(b) and Fig. 4(c) is due to the higher kinetic energy of ablated atoms and ions in vacuum and their more effective energy transfer at near normal incidence, which apparently causes some film-substrate mixing at the interface.

Earlier in situ ion probe measurements revealed most probable velocities of ~0.8 × 10^6 cm/sec in vacuum for Zn and Te ions produced by KrF (248 nm) laser ablation of a ZnTe target at ~0.7 J/cm^2 [5,12]. The atomic weights of Cd, Se, Zn, and Te are respectively 112.41, 78.96, 65.38, and 127.6 g/mole [13], and the collision cross sections calculated from kinetic theory for Ar and N_2 differ by < 10% [14]. Consequently, the velocities of Cd and Se in the ablation plume can be assumed to be similar to those of Zn and Te. A velocity of 10^6 cm/s corresponds to Cd and Se kinetic energies of ~58 eV and ~41 eV, respectively, which is more than enough to displace substrate atoms from their lattice sites. However, the kinetic energy of the incident ablated species is attenuated rapidly with increasing ambient gas pressure [15]. When the kinetic energy of incident particles falls below the threshold for lattice damage, then near-ideal conditions for low-temperature film growth or surface doping reactions are obtained [12].

For instance, when ZnTe was deposited in ambient N_2 gas by PLD, the most probable kinetic energies of incident Zn and Te species decreased from ~23 eV and ~46 eV to ~1 and ~2 eV, respectively, as the partial pressure was varied from 0 to 50 mtorr [5,12]. Thus, the significant changes in the kinetic energy transfer from ablated species that occur as a function of tilt angle and ambient gas pressure appear to be responsible for the changes in film-substrate interdiffusion shown in Fig. 3 and 4 at constant T_p.

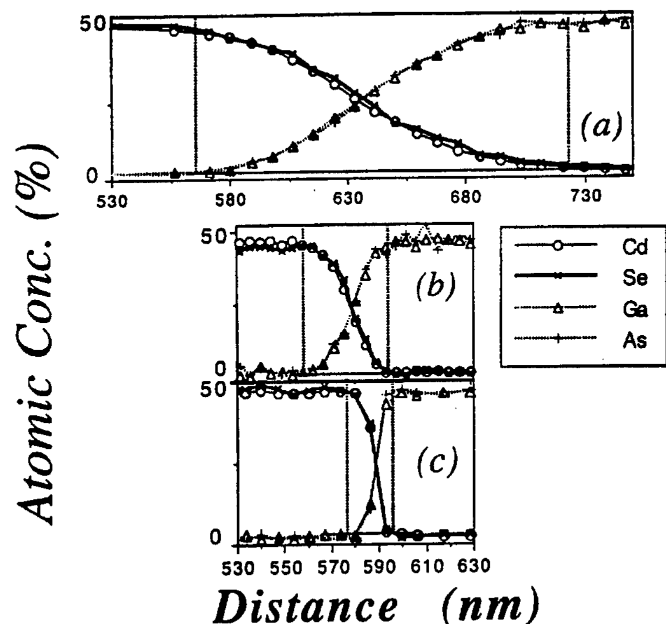

Figure 4. AES depth profiles at the interface of samples; (a) CS2(thickness ~630 nm, T_p = 355°C, Ar gas pressure 50 mtorr),(b) CS4 (thickness ~580 nm, T_p=250°C, in vacuum), and (c) CS7 (thickness ~590 nm, T_p=250°C, Ar pressure 50 mtorr).

The interfacial regions that appear in AES depth profiles also can be artificially broadened during depth profiling by two effects, intermixing [16] and non-uniform sputtering such as sputter roughening of the surface [17–18] or differential etch rate [19]. Bombardment at room temperature with an ion energy as low as the 500 eV used in this work usually does not produce any significant atomic displacements in the near surface region, as estimated by a TRIM calculation [11]. Non-uniform sputtering in the sputter rastering area inevitably results in an artificial apparent interfacial broadening during profiling, especially when the analysis area is large. That is, elements from both the film and the substrate can be detected, because the film and the substrate may co-exist in the analysis area. However, an analysis area only ~0.3 μm in diameter, which was much smaller than the sputter rastering area (100 μm × 100 μm), is believed to have minimized the artificial interfacial broadening induced by non-uniform sputtering. Despite these effects, Figs. 3 and 4 show that considerable interdiffusion took place at the interface governed by changes in the film processing conditions, because the sputtering conditions were the same through out all the analyses.

The interdiffusion shown in Figs. 4(b) and 4(c) is due to the ablated particles bombardment on the substrate surface, but probably is enhanced by defects such as misfit dislocations and microtwins in the film due to large lattice mismatch (7.1%) between CdSe and GaAs. These defects, the kinetic energy of the arriving atoms from the target, and the substrate heating (>250°C) required for the epitaxial growth all may contribute to the observed interdiffusion.

EDS Measurements of Ga and As Diffusion

Figure 5 is a plot of the ratio of the net deconvoluted integrated intensities of Ga and As L x-rays, originating mostly in the CdSe film epilayer, as a function of the substrate temperature. during film growth. The ratio from a GaAs standard (i.e., with no CdSe film) was 1.72. As shown in Fig. 5, no Ga or As L x-rays were detected in this analytical setup from films that were deposited at 250°C to a thickness of ~580 nm (Fig. 5). This shows that very little Ga and As diffused into the CdSe film, therefore most of the Ga and As L x-rays were absorbed as they traveled through the film. On the other hand, for CdSe films grown at T_p = 355°C and 425°C, appreciable Ga and As L x-rays were acquired and the ratios estimated were ~0.7 and ~0.76, respectively, as shown in Fig. 5. The integrated intensity was 2.5 times higher with a ~470 nm thick film than with a ~630 nm thick film, because the Ga and As L x-rays experienced less absorption due to their reduced travel distance through CdSe before escaping. The energies of Ga and As L x-rays are respectively ~1.1 and ~1.3 keV; therefore, slightly more absorption of the Ga L x-ray than of the As L x-ray is expected. However, their effective experimental absorption coefficients do not seem to differ much because the ratio between the integrated Ga L and As L x-rays generated from the films deposited at 350°C were more or less identical regardless of the film thickness. Therefore, the change of the ratio from ~1.72 for the bulk GaAs to ~0.75 for CdSe on GaAs implies that more As atoms than Ga atoms diffused into the CdSe film. The atomic diameters of Ga, As, Cd, and Se are, respectively, 3.62, 2.66, 3.52, and 2.44 Å. Accordingly, replacements of Se by As and of Cd by Ga are expected. However, the numbers of Cd and Se atoms diffusing into the substrate may not be the same as the numbers of Ga and As atoms diffusing into the film, because appreciable numbers of defects such as misfit dislocations and microtwins exist in the films near the interface

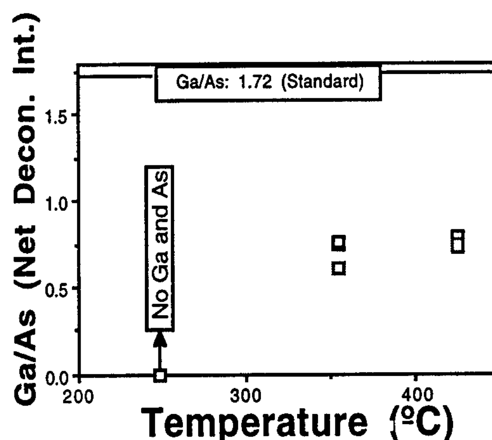

Figure 5. Ratio of the net deconvoluted integrated intensities of Ga and As L x-rays, mostly originating from within the CdSe films, as a function of substrate temperature.

due to the lattice mismatch between CdSe and GaAs. Consequently, as long as the substrate out-diffusion is governed by defects in the film, more As atoms than Ga atoms may diffuse into the film, simply because the atomic diameter of As is smaller than that of Ga.

CONCLUSIONS

These experimental results support the following conclusions:
(i) Film-substrate interdiffusion during heteroepitaxial CdSe/GaAs growth can be largely suppressed by decreasing the growth temperature to ~250°C. (ii) Film-substrate interdiffusion can be reduced further by growing films in a low-pressure ambient gas (e.g., Ar) and by tilting the substrate to be approximately parallel to the ablation plume axis, because each of these reduces the kinetic energy transfer from incident ablated atoms/ions.

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