Crystalline phases of II-VI compound semiconductors grown by pulsed laser deposition

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II-VI compound semiconductors, ZnS, ZnSe, CdS, CdSe, and CdTe, were grown epitaxially on (111) and (100) InP and GaAs substrates by excimer laser ablation. All of these films have good crystalline quality (fully in-plane aligned) and mirror-like surface morphology. It was found that, on (111)-oriented substrates, CdS and CdSe films were in the hexagonal phase with the *c* axis perpendicular to the surface, while ZnS and ZnSe films were in the cubic phase. The films grown on (100)-oriented substrates were all cubic. These high quality films should be useful in optoelectronics applications. © *1994 American Institute of Physics.*

II-VI compound semiconductors are well known for applications in a wide range of optoelectronic devices.[1–3] There has been strong interest in the growth of good quality II-VI compound semiconductors heteroepitaxially on III-V compound semiconductors, especially on GaAs and InP where high quality commercial single crystalline wafers are available. Several techniques had been reported, such as e-beam evaporation,[4] plasma sputtering,[5] hot-wall epitaxy,[6] metalorganic chemical vapor deposition,[7] and molecular beam epitaxy (MBE).[8]

Pulsed laser deposition (PLD) has been used successfully to grow many different materials.[9–13] This technique is fully compatible with MBE sources in an ultrahigh vacuum environment. Single-crystal semiconductor epitaxial thin films have been made by this so-called "laser-MBE" technique.[12,13] The focused pulsed laser beam produces such a rapid temperature rise ($>10^{11}$ K s^{-1}) on the target that the stoichiometry of the target is maintained in the growing film.[14] This is thought to be a way to reduce group VI vacancies, which is the main source of the troublesome native doping in II-VI compounds. High energy atoms and ions in the laser-induced plasma plume create a higher surface mobility which makes it possible to grow high quality films at a relatively low substrate temperature.[12–14] Superlattice or multilayer devices can be easily fabricated by PLD because of its flexibility in using multiple targets. The absence of a high temperature heater in the source region eliminates the necessity of expensive and complicated liquid nitrogen cooling. The drawbacks of PLD are poor film uniformity and surface particles. There are many proposals to tackle these problems. For example, the film uniformity can be improved through the use of scanning techniques and by increasing the substrate to target distance. Uniform deposition on 6-in. wafers has been reported.[15] Operating at a lower laser fluence, longer distance, and off-axis deposition can reduce particle density on the film as well. These improvements can make PLD a viable thin film technique. Recently we reported the deposition of highly doped *p*-type and *n*-type II-VI thin films and the formation of *p*-*n* junctions.[16] In this article, we wish to provide a detailed discussion on the II-VI compound growth process, especially the relation between the grown phase and the substrate orientation. These effects have not been studied carefully in other reports.

II–VI compound thin films were grown on (111) and (100) InP and GaAs substrates by PLD in this study. A clean stainless steel vacuum chamber with a background pressure of 5×10^{-7} Torr was used for the deposition. An ArF excimer laser (Lambda Physik LPX200) at a wavelength of 193 nm and having a pulse duration of 15 ns was focused onto a rotating target at an oblique angle of 30°. The target disk was pressed from pure II–VI compound powder (99.999%) under 8000 lb/cm^2. There was no annealing performed on the target. Substrates were cut from single-crystal wafers and cleaned with trichloroethylene, acetone, and methanol. They were then etched by a H_2SO_4:H_2O_2:H_2O 5:1:1 solution for 30 s and passivated in a $(NH_4)_2S_x$ solution.[17] Before deposition the substrates were preheated in vacuum to 400 °C for 10 min. Growth was performed immediately after cooling down to the growth temperature. During deposition, pure argon (99.999%) was introduced into the chamber through a small gas chamber between the laser window and the target with a flow rate of 40 sccm. This small gas chamber maintained a higher local pressure which shielded the laser window from contamination. The presence of this background Ar during deposition also affects the dynamics of the laser plume and will be discussed later. The gas pressure was changed by partially opening a gate valve to the turbopump for different pumping rates.

Thin film growth was optimized by changing several deposition parameters: (1) the substrate temperature; (2) the laser repetition rate; (3) the laser energy; (4) the focal point size; (5) the substrate-target distance; and (6) the gas pressure. An optimization matrix can be constructed. Generally speaking, the substrate temperature is related to the surface mobility. Optimum crystalline films were obtained at a substrate temperature 300 °C although crystalline films could be formed at a temperature as low as 100 °C. Films deposited at a temperature higher than 400 °C have bad surface morphology and lower group VI ratio from an EDX study. This is consistent with the low sublimation temperature of group VI elements. The laser repetition rate is proportional to the

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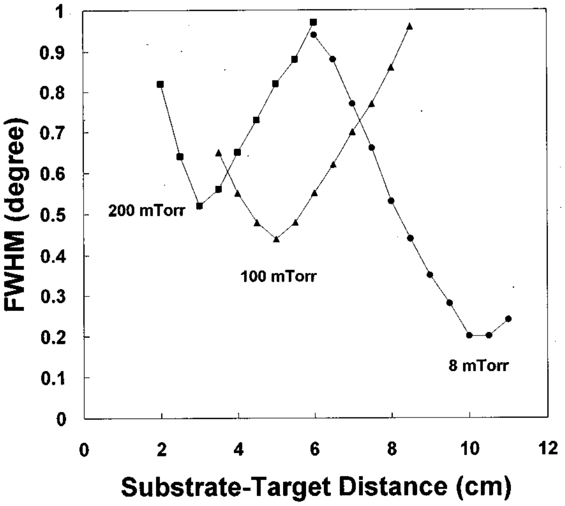

FIG. 1. X-ray rocking curve FWHM of CdS/InP(100) under different deposition conditions.

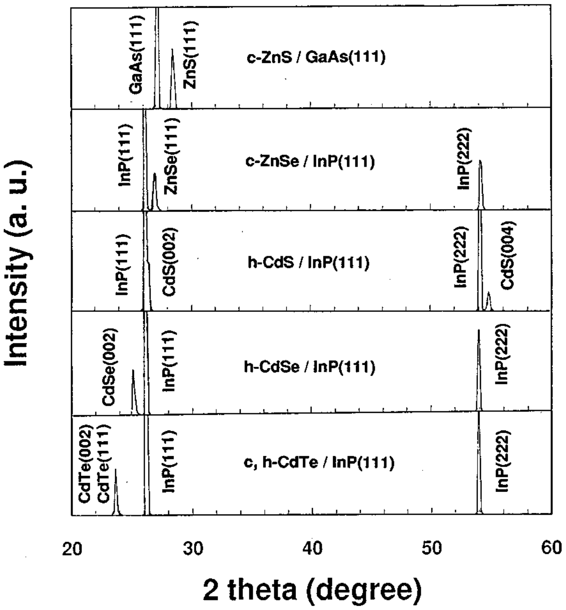

FIG. 2. X-ray 2θ scan of ZnS on GaAs(111); ZnSe, CdS, CdSe, and CdTe on InP(111).

deposition rate. High deposition rates cause defects and bad surface morphology because atoms on the surface need enough time to migrate to the right positions. A repetition rate of 10 Hz was used throughout the present work. All other parameters affect the dynamics of the laser induced plasma plume. For the present study, a laser energy 30 mJ/pulse was delivered on the target with a focal spot size of 2×1 mm^2. This corresponded to a laser fluence of 1.5 J/cm^2. Higher laser fluence resulted in a wider angular distribution and an increase in the surface particle density.

Since we kept all other parameters constant, the two variables in our deposition matrix were gas pressure and substrate-target distance. Figure 1 shows the x-ray rocking curve full width at half-maximum (FWHM) of our CdS thin films on InP(100) substrates at gas pressures of 8, 100, and 200 mTorr with different substrate-target distance. Optimum conditions were obtained at different gas pressures with a specific substrate-target distance. Similar pressure-target distance scaling was found for other II-VI compounds and $YBa_2Cu_3O_{7-\delta}$ depositions.[18] This phenomenon can be interpreted as an optimal atomic energy for the best film growth. Since the background Ar gas collides with atoms in the plasma plume and reduces their kinetic energy, the optimized distance became longer for lower deposition pressure. For short distance deposition, the deposition rate was higher and the uniformity was poorer. As seen in Fig. 1, the best films were obtained at 8 mTorr argon background at a target distance of 10 cm. The deposition rate was 0.05 Å/pulse as measured by a profilometer. These films had a uniformity of within 5% variation in a 1-diam region without substrate rotation. It should be noted that the Ar gas environment is not a necessity here. In fact, Fig. 1 implies that better films with even narrower FWHM may be obtained in vacuum at large target-substrate separations. For applications where reflection high-energy electron diffraction is needed, better optimized deposition conditions can be obtained by tuning the laser fluence and increasing the substrate-target distance at the expense of lower deposition rate. For example, an optimized ZnS deposition condition was achieved in vacuum with a 10 cm target distance and at 1.2 J/cm^2 laser fluence.

There are two major crystalline structures for ZnS, ZnSe, CdS, CdSe, and CdTe—the 2H wurtzite structure (hexagonal phase) and the 3C zinc-blende structure (cubic phase).[19] The band-gap differences of these two phases are too small to be easily distinguished through optical methods. InP and GaAs have a 3C zinc-blende structure. (111) directed cubic substrates can have a lattice match with (001) directed hexagonal thin films because the (111) directed zinc-blende structure still has the sixfold symmetry. The relation between the cubic lattice constant a and the length of hexagon edge L is $a=\sqrt{2}L$. Therefore L is equal to 4.15 Å for InP(111) and 3.998 Å for GaAs(111). Figure 2 shows the x-ray diffraction patterns of ZnS on GaAs(111) substrates; and ZnSe, CdS, CdSe, and CdTe on InP(111) substrates. Because the (111) peaks of the cubic phase and the (002) peak of the hexagonal phase are generally too close (e.g., $d=3.359$ Å for CdS-c and $d=3.3599$ Å for CdS-h), they cannot be distinguished from the 2θ scan of the surface plane. Figure 3 shows the 2θ scans of the CdS (101) plane of the hexagonal phase, which has an angle $\chi=61.91°$ with the surface plane, and the (110) plane of the cubic phase (insert), which has an angle $\chi=35.26°$ with the surface plane. Only the CdS(101) peak was observed. This result proved that the CdS film was in pure hexagonal phase on InP(111) with single in-plane orientation [a axis of CdS parallel with $(1,-1,0)$ direction of InP)]. By using a similar method we found that, on (111)-oriented substrates, the ZnS and ZnSe films were in the cubic phase; CdS and CdSe films were in the hexagonal phase; and CdTe films were in a mixed phase. X-ray results also proved that all of the films grown on (100)-oriented substrates were in the pure (100)-oriented cubic phase. Additionally, it was found that the films on glass substrates were similar to (111)-

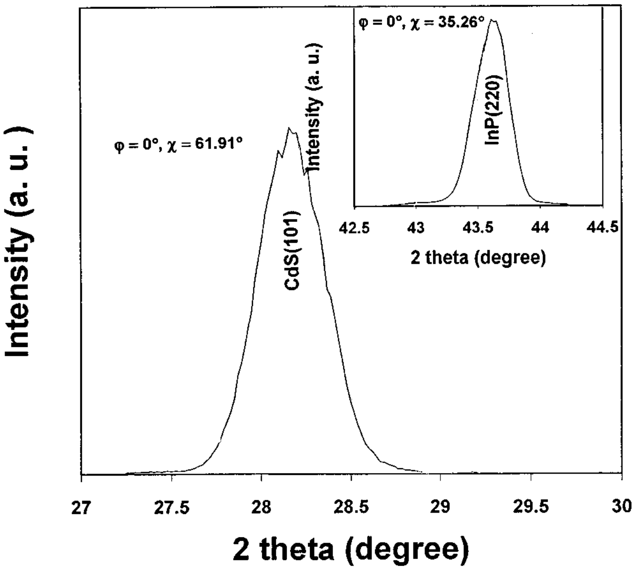

FIG. 3. X-ray 2θ scan on the hexagonal (101) plane ($\varphi=0°$ and $\chi=61.91°$) of a CdS thin film grown on an InP(111) substrate. The insert shows the x-ray 2θ scan on the cubic (110) plane ($\varphi=0°$ and $\chi=35.26°$). The results proved that the Cd film is pure hexagonal phase.

directed substrates. However, all of the films on glass substrates have random in-plane orientation. The phase and orientation were not sensitive to deposition conditions. The x-ray rocking curve FWHM and the film phases are summarized on Table I. Better lattice-matched films are seen to have smaller rocking curve widths as expected. For ZnS on InP, films with no in-plane alignment were obtained. This was attributed to the large lattice mismatch between ZnS and InP.

Photoluminescence (PL) measurements were performed to check the band gap of deposited films by using a spectrometer equipped with an optical multichannel analyzer (EG&G Princeton Applied Research, model 1460). The resolution of the spectrometer was 0.5 nm. An UV nitrogen laser was used as the light source. A helium close-cycle cryosystem was used to cool the samples. The PL spectra of a CdS film on InP(111) at different measurement temperatures are presented in Fig. 4. The peak positions are at 512 nm (2.42 eV) at room temperature and 499 nm (2.48 eV) at 13 K, respectively. These values are in agreement with the known band gap of CdS. The rather wide low temperature PL peak was attributed to impurity states and defects from the grain structure. For applications where single-crystal quality and low impurity density are needed, performing PLD in an ultrahigh vacuum environment is necessary.

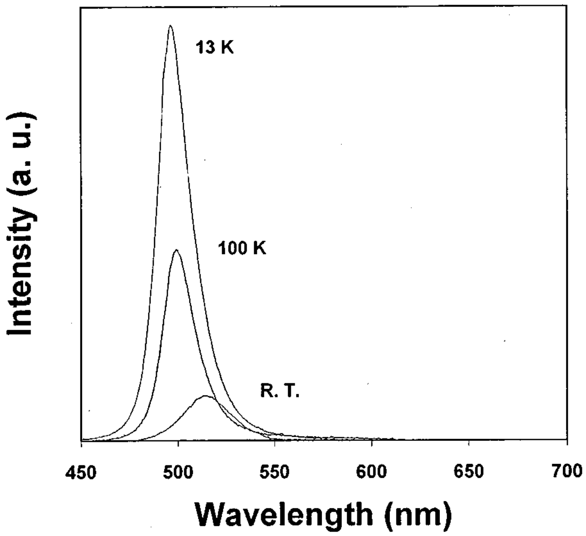

FIG. 4. PL spectra of CdS/InP(111) at different measurement temperatures.

In conclusion, ZnS, ZnSe, CdS, CdSe, and CdTe thin films were grown on (111)- and (100)-oriented InP and GaAs substrates by PLD. The crystalline properties of these films were checked by x-ray diffraction. The crystalline structures on (111) substrates were different with those on (100) substrates. The PL spectrum shows a clear band-edge emission peak which can be used to determine the band gaps of these films.

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TABLE I. The x-ray rocking curve and thin film crystalline phases.

	InP(111)[a]	InP(100)	GaAs(111)	GaAs(100)	Glass
ZnS	C, 10°	C, 10°	C, 0.4°	C, 0.4°	C, 10°
ZnSe	C, 0.4°	C, 0.4°	C, 0.2°	C, 0.2°	C, 9°
CdS	H, 0.3°	C, 0.2°	H, 0.4°	C, 0.5°	H, 8°
CdSe	H, 0.4°	C, 0.4°	H, 0.5°	C, 0.5°	H, 9°
CdTe	Mixed	C, 0.5°	Mixed	C, 0.6°	Mixed

[a] C: cubic phase, H: hexagonal phase.

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