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SUPERLATTICES WITH CONTINUOUSLY VARIABLE
COMPOSITION BY PULSED-LASER ABLATION**

J. W. McCamy* and Douglas H. Lowndes

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*Dept. of Materials Science and Engineering
The University of Tennessee,
Knoxville, TN 37996-1200

Solid State Division
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831-6056
managed by
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GROWTH OF EPITAXIAL SEMICONDUCTOR ALLOYS AND SUPERLATTICES WITH CONTINUOUSLY VARIABLE COMPOSITION BY PULSED-LASER ABLATION

J. W. McCamy

Dept. of Materials Science and Engineering, The University of Tennessee,
Knoxville, TN 37996-1200

Douglas H. Lowndes

Solid State Division, Oak Ridge National Laboratory,
Oak Ridge, TN 37831-6056

ABSTRACT

We describe a new method to grow epitaxial semiconductor alloys with continuously variable composition, while using a single pulsed laser ablation target of fixed composition. Epitaxial $\text{ZnSe}_{1-x}\text{S}_x$ films with continuously variable sulfur content " x " were grown by ablating a ZnSe target through low-pressure ambient H_2S gas. The sulfur content was easily controlled by varying the H_2S partial pressure. The composition of $\text{ZnSe}_{1-x}\text{S}_x$ films differs by as much as $x = 0.52$ from the pure ZnSe target. We have used this method to grow heteroepitaxial structures with either continuously graded or periodically repeating, abrupt compositional changes (compositional superlattices). Structures that simultaneously incorporate both types of compositional modulation also have been grown. This development removes the principal barrier to convenient PLA growth of compositionally graded semiconductor thin-film materials, namely that the film and target normally have the same composition. The method appears to have broad application for PLA growth of other compound semiconductor films and heterostructures, as well as for doping individual layers.

INTRODUCTION

The two techniques most often used to grow semiconductor thin films and superlattices are metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). However, pulsed-laser ablation (PLA) has several practical advantages. These include stoichiometric transport of material from the ablation target to the substrate surface, and growth of smooth films.¹ As with MBE, PLA films can be grown with submonolayer precision. Additionally, the composition of a PLA film is readily changed simply by exchanging solid ablation targets. Consequently, strained layer superlattices of two or more materials are easily grown by PLA.² For example, we recently used PLA of polycrystalline targets to grow uniform, fully epitaxial (e.g., in-plane-aligned) zinc sulfide (ZnS) and zinc selenide (ZnSe) thin films and

$(\text{ZnS})_m\text{--}(\text{ZnSe})_n$ strained layer superlattices (SLS) on (001) GaAs.^{3,4} High resolution TEM (HRTEM), x-ray diffraction (XRD), and Rutherford backscattering spectrometry (RBS) showed that ZnS and ZnSe thin films grown by PLA are structurally comparable or superior⁵ to those grown by MOCVD or MBE.

However, for device applications of II–VI materials it is not sufficient that PLA films simply be structurally of high quality. The critical thickness of a $(\text{ZnS})_n\text{--}(\text{ZnSe})_{2n}$ SLS grown on (001) GaAs is less than 40 nm. Consequently, $\text{ZnS}_x\text{Se}_{1-x}$ alloys may be required to reduce strain within the SLS. In addition, a buffer layer consisting of a compositionally graded semiconductor alloy often is needed to relieve strain between the epitaxial SLS structure and the substrate. Finally, it is anticipated that novel II–VI devices can be constructed by bandgap engineering, e.g., by continuously grading or abruptly modulating the semiconducting energy bandgap. Thus, for PLA to be considered competitive with MBE and MOCVD, a capability to compositionally grade multilayers and superlattices must be developed. Using conventional (i.e., multi-target) PLA it is possible to grow alternating layers of different semiconductor alloy compositions. However, it is not easy or convenient to continuously grade layer composition by this method. (We note, though, that by ablating a CdTe target and varying the laser pulse-repetition rate, in an otherwise conventional MBE environment of constant-fluence effusive Te and Hg beams from Knudsen cells, Cheung was able to control the Cd content and grow $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epilayers with any predesigned compositional profile along the growth direction.¹)

In this paper we report a new method for PLA growth of $\text{ZnSe}_{1-x}\text{S}_x$ alloys with continuously variable composition, by ablating a ZnSe target into low-pressure ambient H_2S gas. By varying the H_2S partial pressure we have grown $\text{ZnSe}_{1-x}\text{S}_x$ films whose composition differs by as much as $x = 0.52$ from the (pure ZnSe) target composition. Moreover, we demonstrate that the method can be used to grow epitaxial structures with either continuously graded or periodically repeating, abrupt compositional changes (compositional superlattices). Structures that simultaneously incorporate both types of compositional modulation also have been grown. This method appears to have broad application for PLA growth of other compound semiconductor films and heterostructures with continuously graded changes of composition, as well as for doping⁶ individual layers.

EXPERIMENTAL

Preparation of the (001) GaAs substrates and details of the ablation geometry used to obtain uniform-thickness films have been described elsewhere.^{3–5} The gas-flow system used to control film composition consists of a manifold with three mass flow controllers (0–10 sccm),

growth chamber (2×10^{-7} Torr base pressure), turbomolecular pump (Balzers TPU170), a 25 mm-diam flow control valve (MKS), and a roughing pump (Alcatel corrosive series, 35 SCFM). The pressure within the chamber was regulated by fixing the gas inlet flow rate and controlling the flow rate out of the chamber. Gas flow through the manifold was initiated and stabilized by first establishing a flow into the low vacuum line before setting the flow into the chamber. For $P < 2$ mTorr, the ambient gas pressure was controlled by varying the turbopump's speed; for $P > 2$ mTorr, the control valve was used. In both cases, the pressure feedback signal was provided by a 1 mTorr MKS Baratron capacitance gauge.

A pulsed KrF (248nm) excimer laser beam (~ 35 ns FWHM pulse duration) was passed through an aperture and brought to a vertical line focus on a 2.54 cm-diam polycrystalline ZnSe target (Angstrom Sciences, 99.999+ % purity) using a single $f_L = +50$ cm cylindrical lens. The results reported here were obtained using a focused energy density $E_0 = 0.35$ J/cm² and a target-substrate separation of 10.8 cm. The H₂S gas ambient was used to control the S content, x , of the ZnSe_{1-x}S_x films. Experiments conducted using both pure H₂S and H₂S diluted in He showed that it is the H₂S partial pressure that controls the sulfur content of films (see below). Alloy film studies typically were carried out by first growing a ~ 300 nm-thick ZnSe buffer layer, followed by a ~ 300 nm-thick alloy film. The film-growth rates were monitored *in situ* using the interference oscillations in the intensity of a HeNe (633 nm) laser beam reflected from the upper and lower surfaces of the growing film. For the results reported here, growth rates along the (001) direction were either ~ 0.05 nm/pulse or ~ 0.15 nm/pulse.

X-ray diffraction (XRD) and room temperature photoluminescence (PL) measurements were used to determine the lattice constant and bandgap variation of the alloy films as a function of the H₂S partial pressure. The alloy composition was inferred from the XRD measurements assuming Vegard's law. Secondary ion mass spectrometry (SIMS) was used to determine the compositional profiles of the graded and superlattice films.

RESULTS AND DISCUSSION

A number of epitaxial ZnSe_{1-x}S_x films were grown at a substrate heater temperature $T_g = 325^\circ\text{C}$, a growth rate of ~ 0.15 nm/pulse, and variable H₂S partial pressure. The resulting variation of sulfur content, x , with H₂S partial pressure is shown in Fig. 1. The solid curve in Fig. 1 is a best fit ($\chi^2 = 10^{-4}$) to the equation $x = C_1 + C_2(P_{\text{H}_2\text{S}})^{1/2}$, with $C_1 = -0.003$ and $C_2 = 0.027$. Lattice matching with GaAs requires a sulfur content of $x \sim 0.06$.⁷ The data point at $x = 0.064$ was generated from an attempt to grow an alloy of the $x = 0.06$ composition, by interpolating from the data

points for the other samples grown previously. The good result illustrates the precise compositional control provided by this technique.

Figure 1. Sulfur content inferred from XRD measurements of $\text{ZnSe}_{1-x}\text{S}_x$ alloy film lattice constants vs H_2S partial pressure.

Figure 2 illustrates the corresponding spatial control over composition that can be obtained along the growth (film thickness) direction. A $\text{ZnSe}_{1-x}\text{S}_x$ multilayered structure was fabricated to simultaneously incorporate both continuously graded and successive abrupt, periodic compositional changes. The thickness of each layer was controlled by the number of laser shots, while each layer's composition was determined by the ambient H_2S partial pressure. By alternately switching the gas pressure between two fixed values, and maintaining each pressure for a fixed number of laser shots, epitaxial structures with highly reproducible layer thickness and continuously selectable layer composition could be formed. Similarly, by gradually changing the H_2S pressure, a crystalline film could be grown with continuously graded composition along the growth direction. These are unique capabilities that are not available when using PLA targets of fixed composition. The structure shown in Figure 2 was grown as follows. First, a $\text{ZnSe}_{0.94}\text{S}_{0.06}$ buffer layer was grown, in order to match lattice constants with the (001) GaAs substrate. The sulfur content then was increased to $x = 0.18$ and

Figure 2. (Top two curves) Idealized periodically modulated and continuously graded sulfur compositional profiles. (Bottom curve) Experimental SIMS profile of sulfur content vs depth (see text).

held constant from 0 nm to 165 nm, but with a $\pm 3\%$ compositional modulation superimposed. Next, the average sulfur content was ramped down from 18% (at 165 nm) to 6% (at 600 nm), still with simultaneous compositional modulation of $\pm 3\%$. Finally, a pure ZnSe cap layer was grown. The resulting continuous crystalline structure consists of 35 distinct epitaxial layers (including buffer and cap), with 16.5 modulation periods of 36 nm each. We note that SIMS' depth resolution is $\sim 5\text{--}10$ nm, so the compositional modulation actually achieved probably is more abrupt than is illustrated in Fig. 2.

ZnS and ZnSe have direct bandgaps of $E_g = 3.7$ eV and 2.7 eV, respectively. Thus, photoluminescence measurements can be used to investigate the variation of bandgap with alloy composition (or H_2S partial pressure). Figure 3 shows the room temperature PL intensity vs photon energy for $\text{ZnSe}_{1-x}\text{S}_x$ films with $x = 0$, $x = 0.09$, and $x = 0.18$. The PL peak broadens and the maximum shifts to higher energy as the sulfur content is increased. The shift in peak position is consistent with sulfur substitutionally entering the lattice on the Se sites, while the broadening is consistent with random (disordered) sulfur incorporation. These PL peaks may be due to the donor-acceptor complexes that have been seen in

similar films.⁸ However, if we assume that the PL maximum is close to the band-edge then the alloy composition can be determined independently using the PL data and the room temperature band-bowing parameter of 0.63.⁹ The sulfur compositions determined independently from the XRD and PL measurements are plotted against each other in Fig. 4. The resulting linear behavior indicates that the near-band-edge structure probably is being maintained. However, low-temperature PL is required to show this conclusively.

To determine the rate-limiting step in the $\text{ZnSe}_{1-x}\text{S}_x$ film-growth reaction is not straightforward for PLA growth, since all of the species present (or formed) in the ablation beam are not known at this time. It is not even clear whether the rate-limiting step is a volume (gas-phase) or surface process. If it is a surface process, then the S-to-Se ratio, $x/(1-x)$, is

Figure 3. Room temperature photoluminescence intensity vs photon energy for $\text{ZnSe}_{1-x}\text{S}_x$ films with $x = 0$, $x = 0.09$, and $x = 0.18$.

expected to scale with the ratio of the adsorption-to-desorption rate ratios for S and Se, and to depend on substrate temperature through this ratio.¹⁰ The square-root H_2S -pressure dependence of the sulfur content in films (shown in Fig. 1) can be taken to mean that the reaction is half-order with respect to the H_2S concentration, but it also could be second-order with respect to the sulfur and selenium concentrations, e.g. if a reaction such as

$S_2 \rightarrow 2S$ is rate-limiting. To assist in identifying the rate-limiting step, we grew $ZnSe_{1-x}S_x$ films in a 22 mTorr H_2S ambient at ~ 0.05 nm per laser shot, at various substrate temperatures. If the rate-limiting growth step (i) involves the competition between S and Se filling sites on the column VI sublattice, and (ii) if S and Se have similar adsorption rates but different desorption rates (see Ref. 10), then the temperature dependence of $x/(1-x)$

Figure 4. Sulfur content, x , determined independently from PL (ordinate) and from XRD (abscissa).

should have an exponentially activated (Arrhenius) form with an activation energy determined by the ratio of their desorption rates.^{10, 11} In this case the activation energy for $x/(1-x)$ should be related to the different strengths of the Zn-S and Zn-Se bonds. Figure 5 shows the relationship between $x/(1-x)$ and reciprocal growth temperature. Note that the relative sulfur content of PLA $ZnSe_{1-x}S_x$ films *increases* with increasing temperature, which is *opposite* to the behavior found recently in VPE growth of $ZnSe_{1-x}S_x$ epilayers by hydrogen transport from heated ZnS and ZnSe powders.¹¹ In the VPE experiments, the decrease of sulfur content with increasing substrate temperature is thought to result from the sulfur desorption rate increasing more rapidly with temperature than the

selenium desorption rate. However, the slope of the experimental (lower solid) line gives an activation energy of 0.233 eV for the PLA-grown films. This is in good agreement with the difference between the calculated Zn-S and Zn-Se single-bond energies of 0.98 eV and 0.74 eV, respectively.¹² For comparison, the slope of the dotted curve in Fig. 5 is exactly this difference.

These preliminary results suggest that the quantity $x/(1-x)$ is thermally activated, and that the activation energy does involve the difference of Zn-S and Zn-Se bond energies. However, the dominant (or rate-limiting) step apparently is not desorption alone. Thus, the sparse data available suggest that the PLA and VPE growth processes differ significantly. This conclusion emphasizes the importance of in situ studies in order to understand PLA growth mechanisms, as well as the opportunity that PLA offers to grow heteroepitaxial materials and structures under unique conditions.

Figure 5. Ratio of sulfur (x) to selenium ($1-x$) content as a function of reciprocal temperature. Solid line: Experimental slope of 0.233 eV. Dashed line: Slope corresponding to the difference (0.24 eV) of calculated Zn-S and Zn-Se single-bond energies. The highest-temperature data point is for $x = 0.52$.

CONCLUSIONS

In this work we have demonstrated that PLA can be used to produce either continuously graded or abrupt, periodic changes in the composition of compound semiconductor films, simply by varying the partial pressure of a hydride gas containing one of the film constituents while using an ablation target of fixed composition. This development removes the principal barrier to convenient PLA growth of compositionally graded semiconductor thin-film materials, namely that the film and target have the same, fixed composition. We anticipate that similar chemistry will occur for ambient gas molecules other than hydrides. Similarly, it should be possible to dope semiconductors from the gas phase by this method.⁶ Consequently, this appears to be an entirely general method for growth of other thin-film compound semiconductors, semiconductor alloys, and epitaxial heterostructures based upon them.

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