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Photoreflectance Characterization of Lattice Strain in Wide-Gap Cu-III-VI_2 Epitaxial Layers

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Photoreflectance (PR) has been applied to the heteroepitaxial layers of $CuAlSe_2$, $CuGaSe_2$, $CuAlS_2$ and $CuGaS_2$ grown on the GaAs(100) substrate by metalorganic vapor phase epitaxy. Lattice strain has been characterized based on exciton transition energies (E_A, E_B and E_C) determined by the PR measurements at 77K. For all epilayers, the tensile biaxial strain has been found, which is represented by the crystal field splittings (Δ_{cf}) larger than those of the bulk crystals. The magnitude of Δ_{cf} decreases with increasing epilayer thickness (d_e) and approaches the bulk value. The strained epilayers are considered to be relaxed when d_e exceeds a critical thickness. These results are discussed in terms of the mismatches of the lattice constant and the thermal expansion coefficient between the epilayer and the GaAs substrate. Effect of the biaxial strain on the energy band structure of $CuAlSe_2$ has been discussed based on the tight-binding calculation.

1. INTRODUCTION

Much attention has been paid to the heteroepitaxy of Cu-III-VI_2-type chalcopyrite semiconductors on GaAs and GaP [1]. It is well-known that the mismatches of the lattice constant and the thermal expansion coefficient between the epilayer and the substrate introduce the lattice strain in the epilayers. This lattice strain is known to cause serious degradation of the optoelectronic devices. However, very little has been reported for the stress/strain in the chalcopyrite epilayer. The authors have grown the heteroepitaxial layers of $CuAlSe_2$, $CuGaSe_2$, $CuAlS_2$ and $CuGaS_2$ on GaAs and GaP substrates by means of metalorganic vapor phase epitaxy (MOVPE), and characterized them by photoluminescence (PL) and photoreflectance (PR) methods[2-6]. During these study, the exciton energies for the epilayers are found to be slightly different from those in the bulk crystals. In particular, the crystal field splittings (Δ_{cf}) of the uppermost valence band for the $CuAlSe_2$ epilayers are larger than those of the bulk crystal[5]. These results show the existence of the tensile biaxial stress/strain in the $CuAlSe_2$ epilayer. Similar results have been found for $CuGaSe_2$/GaAs(100)[3,6,7].

In view of these studies, research of stress/strain in the chalcopyrite epilayer is at the starting point. In the present work, the authors would like to introduce the PR characterization of stress/strain performed on Cu-III-VI_2 heteroepitaxial layers. Effects of the residual biaxial strain on the valence band structure in Cu-III-VI_2 epilayers are studied in detail, by both the analysis of the PR and the band calculation based on the semiempirical tight-binding approximation.

2. EXPERIMENTAL

Most of the Cu-III-VI_2 epilayers have been grown by the low-pressure metalorganic vapor phase epitaxy (LP-MOVPE). Epilayers with the c-axis orientation were used in this study.

PR apparatus consisted of a pump light (either 514.5-457.9 nm lines of Ar^+ laser or 325 nm line of He-Cd laser), a probe light (200W, W-light), monochromator (50 cm focal length), lock-in amplifier and photomutiplier [5]. PR measurements have been carried out at 77 K. PR spectra have been analyzed by the third derivative functional form (TDFF) [7].

3. RESULTS AND DISCUSSION

Figure 1 shows PR spectra of $CuAlSe_2$/GaAs(100) and $CuAlSe_2$/GaP(100) together with those for the bulk $CuAlSe_2$ crystal. PR spectra are represented by three transitions (A, B and C) corresponding to the exciton transitions associated with the valence bands (Γ_7, Γ_6 and Γ_7) and conduction band (Γ_6).

Figure 2 shows transition energies (E_A, E_B and E_C) obtained by the PR spectra plotted as a function of the epilayer thickness (d_e) for $CuAlSe_2$/GaAs(100). E_A is fairly smaller than that of the bulk $CuAlSe_2$ crystal for the thin epilayer, while E_B and E_C are almost independent of d_e and the values are close to those in the bulk crystal. As d_e increases, E_A approaches the value of the bulk $CuAlSe_2$ crystal.

In Fig. 3, spin-orbit splitting (Δ_{so}) and crystal field splitting (Δ_{cf}) are plotted as a function of d_e. The $-\Delta_{cf}$ value for $CuAlSe_2$/GaAs(100) is always larger than that of the bulk $CuAlSe_2$ crystal. This value decreases monotonically with d_e and approaches that of the bulk crystal for larger d_e. While, Δ_{so} of the epilayer is almost independent of d_e, which is

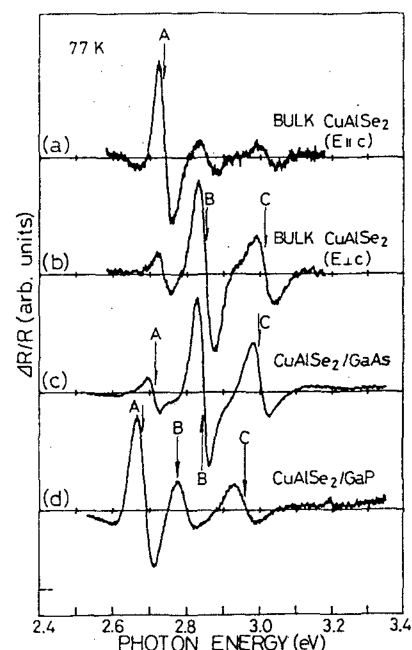

Figure 1. PR spectra of $CuAlSe_2$ epilayers and bulk crystal.

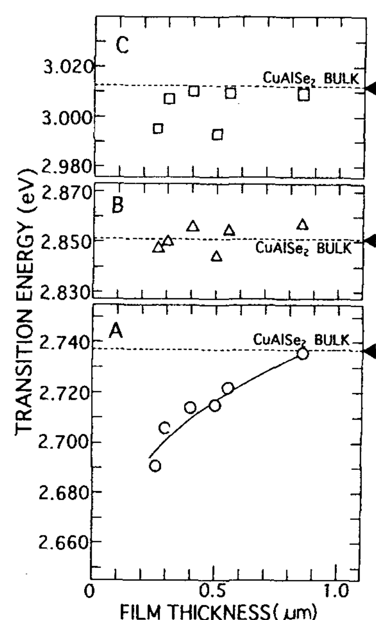

Figure 2. Transition energies plotted as a function of epilayer thickness for $CuAlSe_2$/GaAs(100).

same magnitude as that of the bulk crystal.

This large $-\Delta_{cf}$ value is due to the increase of the tetragonal distortion ($2-c/a$), and the result shows that the epitaxial $CuAlSe_2$ layer suffers the biaxial tensile lattice strain.

The decrease of $-\Delta_{cf}$ with d_e shown in Fig. 3 indicates the relaxation of strain in $CuAlSe_2$ which is larger for the thicker layer because d_e exceeds the critical thickness. The critical thickness h_c has been estimated to be 290 Å using the relationship; $h_c \fallingdotseq b/2f$, where b is the Burgers vector ($b=\sqrt{2}/2a=3.96$ Å) and f is lattice mismatch ($f=\Delta a/a=0.0068$, 300K).

Figure 4 shows the energy difference of E_A between the epilayers grown on GaAs(100) and the bulk crystal plotted as a function of d_e for $CuAlSe_2$, $CuGaSe_2$, $CuGaS_2$, and $CuAlS_2$. For $CuAlS_2$/GaAs(100), E_A was determined by the PL peak. For all epilayer, E_A is smaller than that of the bulk crystal. As d_e increases, E_A of the epilayers approaches to that of the bulk crystal. With d_e of 0.8 μm, most of the strain is considered to be relaxed for the every four heteroepitaxial layers. Therefore, the relaxation of lattice strain with increasing epitaxial layer thickness is considered to be a common tendency of the Cu-III-VI_2-type epitaxial layers grown on the GaAs(100) substrate.

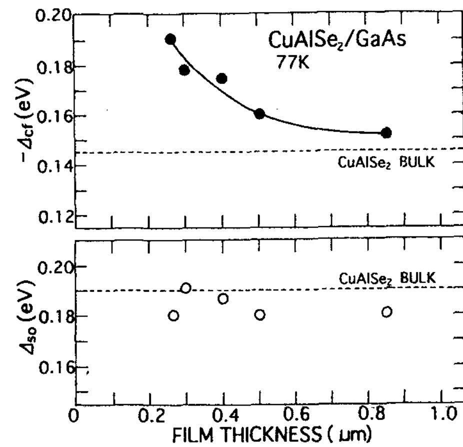

Figure 3. Δ_{cf} and Δ_{so} plotted as a function of epilayer thickness for $CuAlSe_2$/GaAs(100).

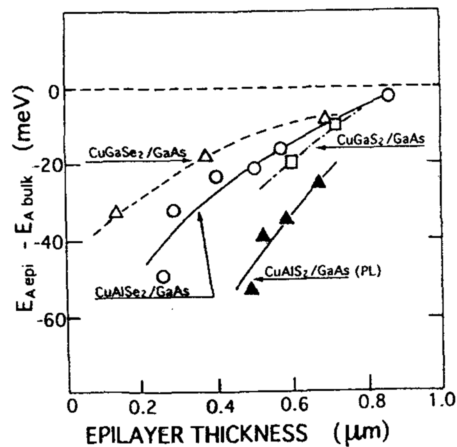

Figure 4. Shift of E_A plotted as a function of epilayer thickness.

Table 1
Lattice mismatches with respect to GaAs and thermal expansion coefficients for Cu-III-VI_2.

	Lattice mismatch (%)		Thermal expansion coefficient (K^{-1})	
	$(a-a_{GaAs})/a_{GaAs}$	$(c/2-a_{GaAs})/a_{GaAs}$	a-axis	c-axis
$CuGaSe_2$	-0.49	-2.2	13.1×10^{-6}	5.2×10^{-6} [8]
$CuAlSe_2$	-0.68	-2.8	13.4×10^{-6}	4.6×10^{-6} [9]
$CuGaS_2$	-5.2	-7.2	11.2×10^{-6}	4.1×10^{-6} [9]
$CuAlS_2$	-5.5	-7.4	13.7×10^{-6}	6.1×10^{-6} [9]
GaAs			5.7×10^{-6}	

Table 1 shows the lattice mismatches and the thermal expansion coefficients of Cu-III-VI_2 compounds. It is expected for $CuAlSe_2$/GaAs and $CuGaSe_2$/GaAs that both the lattice mismatch and the difference of thermal expansion coefficients cause the tensile biaxial strain. For $CuAlS_2$/GaAs and $CuGaS_2$/GaAs, strain is due to the difference of thermal expansion coefficients because the lattice strain is considered to be completely relaxed at growth temperature because of the large lattice mismatch. Therefore, tensile biaxial strain is expected.

In order to clarify the effect of the biaxial strain on the energy band, energy band of $CuAlSe_2$ has been calculated by the semiempirical tight-binding approximation taking the p-d hybridization between Se-4p and Cu-3d and spin-orbit interaction into account.

Figure 5 shows the energies of the valence bands (Γ_7, Γ_6 and Γ_7) and conduction band

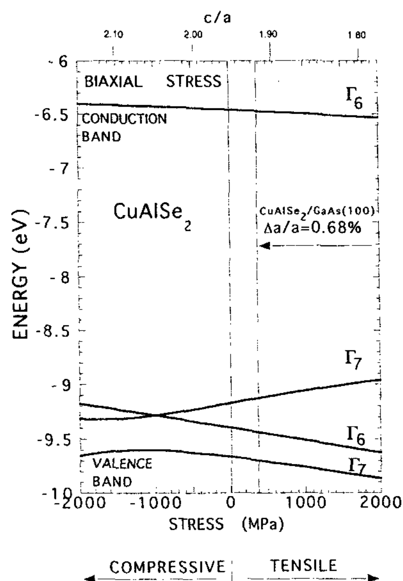

Figure 5. Calculated energies of valence and conduction bands as a function of biaxial stress for $CuAlSe_2$.

(Γ_6) plotted as a function of applied biaxial stress. As tensile biaxial stress increases, energy of the Γ_6 conduction band decreases and the splitting between the upper two valence bands (Γ_7 and Γ_6) increases. Thus, E_A decreases and $-\Delta_{cf}$ increases as tensile stress increases. Based on this calculation, magnitude of Δ_{so} does not change with stress. These results well explain the tendencies of the PR results.

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