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Lattice Strain of Epitaxial $CuGaSe_2$ Layers on GaAs(100) Substrates

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Lattice parameters a and c, and optical transition energies at A, B and C bandgap of $CuGaSe_2$ epitaxial layers grown on GaAs(100) substrates by chloride MBE were measured as a function of temperature.The tetragonal distortion (2−c/a) of the epitaxial crystals was 0.0632 and twice as large as that of bulk $CuGaSe_2$ crystal. The amount of valence band splitting was analyzed by the quasicubic model. The spin−orbit splitting Δ_{so} is 229±2meV, being temperature independent. The crystal−field splitting Δ_{cf} varied from −152meV at 14K to −142meV at 200K due to the temperature variation of the tetragonal distortion. The negative deformation potential b was estimated with the measured values of the tetragonal distortion and found to be −1.5eV with a small temperature dependence.

1. INTRODUCTION

The I−III−VI_2 compound semiconductors crystallize in tetragonal chalcopyrite structure, which is a super lattice of the zincblende structure with an ordered distribution of column I and III atoms. The lattice parameter ratio c/a of most of chalcopyrite semiconductors is slightly smaller than 2 as a result of the cation ordering. The value (2−c/a) is a measure of the tetragonal distortion. The positions of anions in the tetragonal unit cell are also determined by the lattice parameters a and c, if the anions are assumed to be located tetrahedrally around the column III atoms. Therefore, the value of tetragonal distortion (2−c/a) is an important parameter determining the electronic properties of chalcopyrite semiconductors, such as bandgap energies and valence band structures.

Recently, a lot of studies have been made on epitaxial growth of chalcopyrite semiconductors by MBE, MOVPE, chloride CVD, etc. The III−V and II−VI compounds have been used as substrate materials for lack of large area and high quality wafers of chalcopyrite compounds. The heteroepitaxial layers are strongly strained due to the mismatches of lattice parameters and thermal expansion coefficient between the grown layers and substrate materials. As a result, the values of the tetragonal distortion of heteroepitaxial crystals differ from those of bulk crystals. The distortion varies with temperature due to the mismatch of thermal expansion coefficients, and with layer thickness due to the relaxation of lattice strain by introducing misfit dislocations. The value of tetragonal distortion of bulk crystals also change with temperature because of the difference in thermal expansion along the a and c axis. The temperature variation of the tetragonal distortion of heteroepitaxial layers is a function of over grown material, substrate material, growth orientation and grown layer thickness , and it is more complicated than that of bulk crystals.

In this paper we describe the temperature dependence of the value of tetragonal distortion and the energy gaps at A, B and C banbgaps of $CuGaSe_2$ epitaxial layers grown on GaAs(100) substrates. The valence band structure is analyzed by the quasicubic model and discussed with reference to the bulk $CuGaSe_2$ crystal.

2. EXPERIMENTS

$CuGaSe_2$ epitaxial layers were grown by the chloride MBE[1]. Source materials CuCl, Ga and Se, were supplied from resistive heated Knudsen-type cells with temperatures of 205~240℃, 810~950℃ and 150~180℃, respectively. GaAs(100) wafers were used as substrates. Mirror polished wafers were etched in a solution of $5H_2SO_4+H_2O_2+H_2O$ at 60℃ for 15s and treated in $(NH_4)_2S_x$ solution for 3m just before setting in the growth chamber. The substrate temperature was in the range of 650~760℃. A high purity nitrogen gas was introduced into the growth chamber with a pressure of 2×10^{-5}Torr as a buffer gas. Epitaxial growth with the c axis of $CuGaSe_2$ normal to the substrate surface was obtained under the above mentioned conditions. The quality of grown layers depends on the source flux ratios CuCl/Ga and Se/(CuCl+Ga) and the substrate temperature, and the details will be reported elsewhere. The tetragonal distortion of the epitaxial layers was estimated by X-ray diffraction technique in a temperature range of 100~300K. The lattice parameter c was determined from the (008) symmetric reflection peak of $CuGaSe_2$, and the lattice parameter a was calculated from the peak position of the (408) asymmetric reflection of $CuGaSe_2$ and the value of c. Optical reflection spectra were measured on the as-grown surfaces of $CuGaSe_2$ layers in a temperature range of 10~300K. Electronic transition energies were determined from the dip position in the spectra obtained by numerical derivative of the reflection spectra.

3. RESULTS AND DISCUSSION

Figure 1 shows the layer thickness dependence of the room temperature lattice parameters a and c of $CuGaSe_2$ epitaxial layers on GaAs(100) substrates. When the layer thickness is smaller than 300~400nm, a is 5.653 Å and c is 10.948Å, being almost thickness independent. The value of a is equal to the lattice parameter of the GaAs substrate. When the layer thickness increases over a critical thickness, the elastic strain in grown layers is relaxed by introducing misfitdislocations and the lattice parameter a and c respectively decreases and increases with increasing layer thickness, approaching to the balk value of $a_{bulk}=5.61$Å and $c_{bulk}=11.03$Å, as can be seen in Figure 1. The critical thickness of coherent growth of $CuGaSe_2$ on GaAs(100) substrates was found to be about 300nm. The value of the tetragonal distortion (2-c/a) of $CuGaSe_2$ coherently grown on GaAs (100) is calculated to be 0.0632, which is twice as large as that of bulk $CuGaSe_2$.

The lattice parameter a and c of 200nm thick epitaxial layers were measured in a temperature

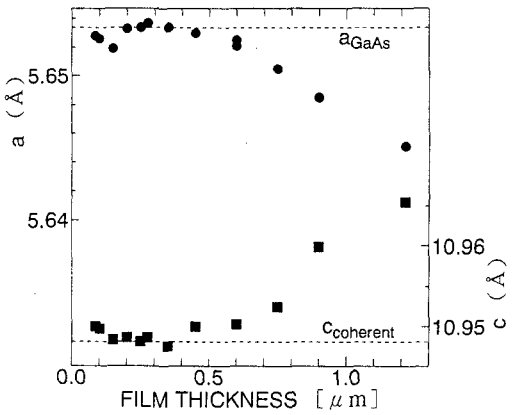

Figure 1. Layer thickness dependence of lattice parameter a and c of $CuGaSe_2$ on GaAs(100).

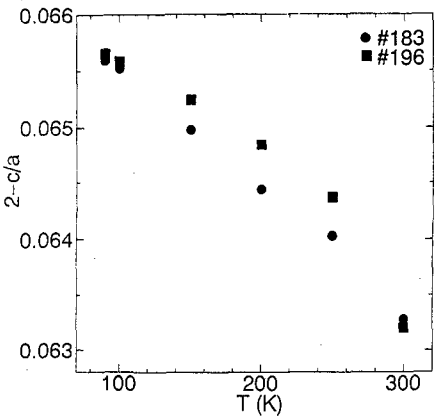

Figure 2. Temperature dependence of tetragonal distortion of coherent $CuGaSe_2$/GaAs(100).

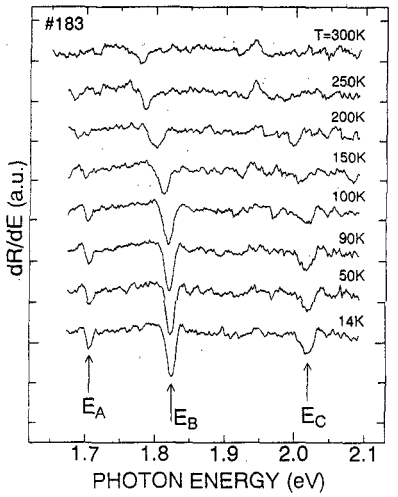

Figure 3. Reflection spectra of $CuGaSe_2$/GaAs(100).

range of 100 to 300K, and the lattice parameter a was found to be very close to the GaAs lattice constant in the whole temperature range [2]. The observation confirmed the lattice coherency between $CaGaSe_2$ layers and GaAs substrates. Figure 2 shows temperature dependences of the tetragonal distortion of two coherently grown samples. The quantity (2−c/a) decreases from 0.0656 to 0.0632 with increasing temperature from 100 to 300K. The tetragonal distortion of $CuGaSe_2$ bulk crystal is expected to increase from 0.031 at 100K to 0.034 at 300K, because the thermal expansion coefficient along the a axis($13.1\times10^{-6}K^{-1}$) is larger than that along the c axis($5.2\times10^{-6}K^{-1}$).

Figure 3 shows numerical derivatives of reflection spectra of a $CuGaSe_2$ epitaxial layer at different temperatures. The temperature dependence of the amount of the tetragonal distortion of the sample is given in Figure 2. Three dips corresponding to the electronic transitions at the A, B and C bandgap are observed in each spectrum, being positioned respectively at 1.705, 1.825 and 2.020eV at 14 K. The temperature dependences of the transition energies are given in Figure 4.

According to the quasicubic model [3], the splitting of p−like valence band of the chalcopyrite semiconductors with tetragonal distortions is expressed as

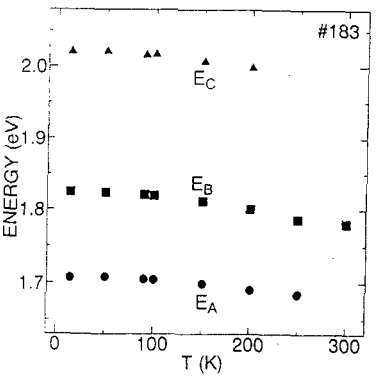

Figure 4. Temperature dependence of E_A, E_B and Ec of $CuGaSe_2$/GaAs(100).

$$E(\Gamma_7)-E(\Gamma_6)=-\frac{1}{2}(\Delta_{so}+\Delta_{cf}) \pm \frac{1}{2}\{(\Delta_{so}+\Delta_{cf})^2-\frac{8}{3}\Delta_{so}\Delta_{cf}\}^{1/2} \quad (1)$$

where Δ_{so} is spin−orbit splitting of the valence band under a crystal field of cubic symmetry and Δ_{cf} is crystal−field splitting of the valence band in the absence of spin−orbit interaction.

Figure 5 shows Δ_{so} calculated using equation (1) at different temperatures. The spin−orbit splitting Δ_{so} is temperature independent, and is 229 ± 2meV in the whole measured temperature range of 14~200K. The value is equal to the spin orbit splitting of 0.23eV observed for $CuGaSe_2$ bulk crystals. This observation suggests that Δ_{so} is insensitive to the tetragonal distortion. Similar insensitiveness of Δ_{so} to lattice strain has been reported for $CuAlSe_2$ [4].

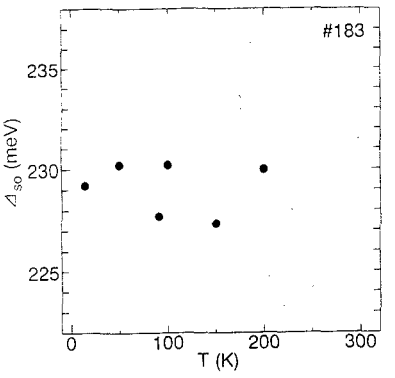

Figure 5. Temperature dependence of Δ_{so}.

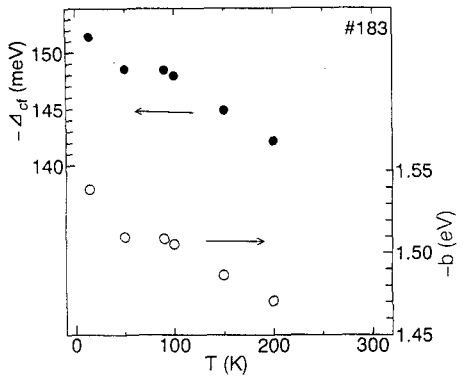

Figure 6. Temperature dependences of Δ_{cf} and deformation potential b.

On the other hand, a distinct temperature dependence was observed in the crystal field splitting, as can be seen in Figure 6. The Δ_{cf} of bulk $CuGaSe_2$ crystal is about 0.1eV. The difference between heteroepitaxial layer and bulk crystal is expected due to the difference in the quantity of the tetragonal distortion. In the quasicubic model, which predicts that uniaxial compression of binary zincblende compound is responsible for a negative crystal-field splitting of ternary chalcopyrite compound, Δ_{cf} is given by

$$\Delta_{cf}=\frac{3}{2}\, b\,(2-\frac{c}{a}) \qquad (2)$$

where b is called (negative) deformation potential[3]. The deformation potential b was calculated to be -1.51eV at 100K by equation (2). Figure 6 includes the temperature dependence of b. The deformation potential of bulk $CuGaSe_2$ is calculated to be -1.7eV using $\Delta_{cf}=-0.1$eV and $(2-c/a)=0.04$. This value is approximately same as those given in Figure 6. Recently, Shirakata[5] measured Δ_{cf} on bulk $CuGaSe_2$ grown by iodine transport method over a temperature range of 4~290K, and found that $-\Delta_{cf}$ decreases with increasing the temperature. The temperature dependence was very similar to that of Figure 6. The tetragonal distortion of bulk $CuGaSe_2$ has an opposite temperature dependence to that of $CuGaSe_2$ layers coherently grown on GaAs(100) substrate as mentioned before. Therefore, equation (2) would give a much stronger temperature dependence of the deformation potential b for $CuGaSe_2$ bulk crystals than $CuGaSe_2$ layers on GaAs(100) substrate. A similar observation was reported on bulk and epitaxial $CuAlSe_2$ system[4].

The Δ_{cf} is a characteristic parameter of chalcopyrite semiconductors, and its value is very sensitive to lattice strain. In order to make more detailed discussions on the effect of the tetragonal distortion on the valence band structure, it seems necessary to know values of lattice parameters a and c for the exact position of a sample on which Δ_{so} and Δ_{cf} are measured.

4. CONCLUSION

The lattice parameters and the tetragonal distortion $(2-c/a)$ were measured in a temperature range of 100~300K on $CuGaSe_2$ layers grown coherently on GaAs(100) substrates by chloride MBE. The temperature dependent valence band structure was measured and compared with bulk $CuGaSe_2$. The Δ_{so} was 230meV, which is same as that of bulk crystal and independent of temperature. The Δ_{cf} was larger than that of bulk crystal because of larger tetragonal distortions. Effects of crystal quality on measured value of the deformation potential b were discussed.

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