Control of Composition Profile in Mercury Cadmium Telluride Films Prepared by Isothermal Vapor Phase Epitaxy

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Hg_{1-x}Cd_xTe (MCT) films were grown by using three kinds of source materials on conventional open tube isothermal vapor phase epitaxy. The composition profile was dependent on the source materials: HgTe and sintered MCT sources resulted low x thick film and high x thin film, respectively. By considering these effects, the mixture sources of HgTe and CdTe enabled to produce the films of flat composition profile with $x \approx 0.2$ and thickness of 10 μm .

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I. Introduction

Mercury cadmium telluride (MCT, Hg_{1-x}Cd_xTe) is widely used for infrared devices. The isothermal vapor phase epitaxy (ISOVPE) method has been considered to be the simplest and least expensive method among epitaxial methods (i.e. MBE, MOCVD, LPE). It has also the potential to produce films with high device quality⁽¹⁾⁻⁽⁴⁾, since it is close to equilibrium growth and surface morphology is excellent. For high performance of the photodiode, the MCT film must be kept flat in composition profile at surface region and at 10–15 μm in thickness, which is on the order of a minority-carrier diffusion length⁽⁵⁾. There have been a number of modifications of this growth method in order to satisfy these requirements⁽¹⁾⁻⁽⁴⁾⁽⁶⁾, but successful results have not been achieved.

The present study reports control of composition profile of MCT with $x \approx 0.2$ on CdTe substrate by open tube ISOVPE.

II. Experimental

1. Preparation of source materials

The source materials, HgTe and CdTe, for the following ISOVPE experiments were prepared by direct reaction of the constituent elements. HgTe crystal boules were grown by the Bridgman method after synthesizing by direct reaction using Hg and Te (nominal purity, 99.9999%) with 5 at% excess Hg from stoichiometric composition. In order to avoid deviation from the stoichiometric composition, the HgTe crystals (~3 mm in diameter) cut from the boules were annealed in Hg atmosphere at 773 K with the Hg reservoir temperature of

673 K, where the condition corresponds to the p-n boundary⁽⁷⁾ in the P-T phase diagram⁽⁸⁾.

Figure 1 shows the conventionally designed apparatus for ISOVPE growth referred to the literature⁽¹⁾. The reactor is composed of an outer quartz tube and an inner tube with a push rod, which are connected with the ground joint each other. The substrates (CdTe wafers) and the source materials are placed in a graphite boat. The growth well and the reservoir contain the same source material (the amount: 0.5 g in the growth well and 2 g in the reservoir).

In a growth run, the reactor is filled with slowly flowing high purity hydrogen (100 sccm) at atmospheric pressure after N₂ introduction and evacuation. In the first stage of heating the growth chamber, the inner tube is loosely set in the outer one to allow the escape of expanding gases. When the temperature reaches 523 K, the assembly is completely closed by pushing the rod to prevent Hg loss. The growth chamber is heated up to the growth temperature in 30 min. The growth condition are; temperature: 723 ~ 773 K and growth period: 2 ~ 20 h. Three kinds of sources were used as the starting materials; (i) block form HgTe crystals, (ii) sintered Hg_{1-x}Cd_xTe ($x=0.2$ and 0.3) and (iii) a mixture of block form HgTe

Fig. 1 ISOVPE growth system of MCT film; a: source material, b: reservoir material, c: substrate, d: spacer, e: cap, f: inner tube, g: outer tube, h: push rod and i: thermocouple.

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and CdTe (less than 2 mm in diameter) with $r = 0.05 \sim 0.20$ for $(1-r)\text{HgTe}:r\text{CdTe}$. After the growth, the temperature was lowered in 1 h to room temperature.

Prior to the growth run, the Hg evaporation loss experiment was performed at 723 and 773 K using the same boat and heating system as that used for ISOVPE. The source material decreased in its weight monotonously with time, and changed into the liquid phase until the decrease was beyond 30% of the initial weight. The result indicates that the source material changed by Hg evaporation from the HgTe to Te-rich liquidus alloy, passing through the two-phase alloy (solid HgTe and a Te-rich melt). The grown film did not change immediately into melt after the melting of the source, which suggests that the MCT film might have continued to grow as far as Hg vapor pressure is in the region out of HgTe and within MCT⁽⁹⁾. The specular MCT film resulted in the region within 30% loss, while the surface became gray in the region more than 40% loss. Therefore the growth period was limited within that of the 30% weight change of the initial source weight (e.g., for 6 h at 773 K and 28 h at 723 K).

The composition profiles of the films were measured by electron probe microanalysis (EPMA) with the wavelength dispersive spectroscopic mode. The standards used for the analysis were HgTe and CdTe crystals.

III. Results and Discussion

Figure 2 shows the composition profile obtained by using the HgTe source(i). The prolonged heating results thicker layer and smaller x value. The film thickness is about $20\ \mu\text{m}$, while the surface composition is low lying at $x \approx 0.1$. The film thickness follows $t^{1/2}$ dependence (t : time), which corresponds to the interdiffusion limited process⁽⁶⁾. The goal composition ($x=0.2$) at the surface could be attained by grinding of the layer up to $14\ \mu\text{m}$, which will not produce flat composition profile necessary in designing the IR device.

Figure 3 shows the composition profile obtained by using the sintered source (ii) with $x=0.3$. The large x

Fig. 2 Composition profile of MCT film grown at 773 K for 5 h by using HgTe source.

Fig. 3 Composition profile of MCT film grown at 723 K for 5 h by using sintered MCT source ($x=0.3$).

Fig. 4 Composition profile of MCT film grown at 773 K for 15 h by using a mixture source of 0.85HgTe and 0.15CdTe.

value at surface and thin film resulted, suggesting that the rate of Hg deposition was lower than that of Cd interdiffusion into the MCT films because the Hg pressure of the sintered MCT source is smaller than that of HgTe.

Figure 4 shows the composition profile obtained by using a mixture source (iii). The surface composition is close to 0.2 and the layer thickness is $10\ \mu\text{m}$. Figure 5 shows the relationship between surface composition and the source composition r of the mixture $[(1-r)\text{HgTe}:r\text{CdTe}]$. The surface composition increases with the increase of the source composition. The surface composition also increases with the increase of the growth temperature. The results suggest that the surface composition might be determined by both Cd diffusion from the substrate into the film and Hg evaporation from the source.

Figure 6 shows that surface composition increases with an increase of growth period in the measured range. From these results, the composition profile of the MCT film is found to depend upon the source material, where the optimum condition is; a mixture source of 0.85HgTe:0.15CdTe, growth temperature: 773 K and growth period: 15 h.

Among the three kinds of the source materials, HgTe

Fig. 5 Plots of surface composition versus source composition r in the mixture of $(1-r)\text{HgTe}$ and $r\text{CdTe}$ with the heating period of 5 h and at temperatures of (●): 773, (○): 790 and (□): 823 K.

Fig. 6 Plots of surface composition versus growth period; source composition r in the mixture of $(1-r)\text{HgTe}$ and $r\text{CdTe}$: 0.10 (●) and 0.15 (○), growth temperature at 773 K.

source (i) is favorable to thick film and MCT one (ii) to high x value. The mixture source (iii) seems to have the advantages of both the sources (i) and (ii). The growth process in the case of the source (iii) can be considered as follows: at first step, the predominant Hg and Te_2 evaporation from HgTe in the source material mixture; as the reaction between HgTe and CdTe proceeds in the growth process, the resultant MCT causes an increase of the x value of the film. The detailed growth mechanism must be analyzed under the consideration of Hg evaporation loss and the interdiffusion inside the film.

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REFERENCES

- (1) J. Piotrowski, Z. Djurić, W. Galus, V. Jović, M. Grudziński, Z. Djinović and Z. Nowak: *J. Cryst. Growth*, **83** (1987), 122.
- (2) S. B. Lee, L. K. Magel, M. F. S. Tang, D. A. Stevenson, J. H. Tregilgas, M. W. Goodwin and R. L. Strong: *J. Vac. Sci. Technol.*, **A8** (1990), 1098.
- (3) J. Piotrowski, Z. Nowak, M. Grudziński, W. Galus, K. Adamiec, Z. Djuric, V. Jovic and Z. Djinovic: *Thin Solid Films*, **161** (1988), 157.
- (4) O. de Melo, A. Attolini, F. Leccabue, R. Panizzieri, C. Pelosi and G. Salviati: *J. Cryst. Growth*, **98** (1989), 704.
- (5) M. B. Reine, A. K. Sood and T. J. Tredwell: *Semiconductors and Semimetals*, Vol. 18, ed. by R. K. Willardson and A. C. Beer, Academic Press, New York, (1981), p. 201.
- (6) J. G. Fleming and D. A. Stevenson: *J. Cryst. Growth*, **82** (1987), 621.
- (7) T. Kagotani: *Bull. Japan Inst. Metals*, **49** (1985), 243.
- (8) R. F. Brebrick and A. J. Strauss: *J. Phys. Chem. Solids*, **26** (1965), 989.
- (9) Z. Djuric, Z. Djinovic, Z. Lazic and J. Piotrowski: *J. Electron. Mater.*, **17** (1988), 223.