Volume 4, Number 8
1004-423X/95/04080606-06

ACTA PHYSICA SINICA
(Overseas Edition)

August, 1995
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PHOTOLUMINESCENCE STUDY ON $Hg_{1-x}Cd_xTe$ THIN FILM IMPLANTED WITH As ION

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(Received 21 September 1994)

Photoluminescence spectra of a series of MBE-grown $Hg_{1-x}Cd_xTe$ samples with the same mole fraction of about $x \approx 0.39$ have been measured at different temperatures from 5 to 100 K. By aid of the temperature and exciting laser power dependence of photoluminescence peak energy and relative intensity, as well as of the comparison with other measurements, four main structures dominating in the photoluminescence spectra are attributed to band to band, D^oX, A^oX and D^oA^o transitions. A deep donor state level located at about 8.5 meV below the bottom of the conduction band has been observed and is determined to be due to the arsenic-occupied mercury vacancies. Two acceptor levels located at about 14.5 meV and about 31.5 meV above the top of the valance band have also been found from the measuements, which are identified as the mercury vacancies and As in anion site, respectively.

PACC: 7155; 7855; 7865

I. INTRODUCTION

The thermal imaging applications require large-area arrays of infrared (IR) detectors and increasingly the emphasis is switching from using the photo-conductive effect to the photo-voltaic effect because of power dissipation problems. The n-type $Hg_{1-x}Cd_x$ films grown by molecular beam epitaxy (MBE) are widely used in fabricating the photo-voltaic infrared detector arrays because of their good performance under current conditions. To produce the necessary p-n junction, the film is implanted with As and then annealed at a suitable temperature to induce the As-occupied anion site so as to get p-type layers. The successful application of these conversion processes relies on the knowledge of impurity behavior in the materials; consequently, the study on the impurity and defect states in the As-implanted $Hg_{1-x}Cd_xTe$ films is a significant work.

In this paper, we report the investigation of a series of MBE-grown samples, in which all have the same mole fraction of about $x \approx 0.39$ and the same implantation conditions but annealed at different temperatures. The investigations mainly take advantage of photoluminescence spectroscopy, which is proved to be a suitable means to study the impurity and defect states in semiconductors.[1] From the experimental facts, the origin of the main

structures was obtained and the following results were inferred: The As ions implanted in MBE-grown $Hg_{1-x}Cd_xTe$ ($x \approx 0.39$) can occupy the anion site to induce a 31.5 meV acceptor level above the top of valance band, and can occupy the mercury vacancies to lead to a 8.5 meV donor level below the bottom of conduction band as well.

II. EXPERIMENTAL

The samples prepared for the experiment were cut from the same piece of As-implanted $Hg_{1-x}Cd_xTe$ thin film grown in a FW-III MBE equipment on GaAs substrate with a 5 μm CdTe buffer layer. They were then annealed under a suitable Hg pressure at different temperatures: sample 1 annealed at 450°C, sample 2 at 400°C and sample 3 at 350°C.

In the photoluminescence experiment an Oxford CF 1204 continuous flow liquid helium cryostat was employed. The sample was emerged in cold helium gas. The temperature was measured by a sensor positioned a few millimeter above the sample. A heater was installed to accurately control the temperature which can be varied from 1.6 K to room temperature. The Ar^+ laser (514.5 nm) was used as an exciting source and the photoluminescence signals from the sample were collected by a paraboloid mirror, and then fed into the Nicolet 800 Fourier transform infrared (FTIR) spectrometer for processing, with an energy resolution of 0.5 meV.

The photoluminescence experiment was first performed on the As-implanted samples. After that, the samples were etched in HBr solution to remove the doped layer for the next measurement.

For comparison, the transmission measurements were also performed for each sample, before and after etching.

III. RESULTS AND DISCUSSION

Figure 1 shows the transmission spectra of sample 1 (annealed at 450°C) before and after etching. From the spectra, one can obtain that the surface composition x is about 0.394 and the thickness of the film is about 10 μm (before etching) or 7 μm (after etching) according to the methods given in Refs.[2–4]. It can be seen that the film thickness of sample 1 decreases by 3 μm after etching. The results of secondary ion mass spectroscopy (SIMS) measurements for the samples, whose implantation and annealing conditions are the same as that for sample 1 show that the As doping concentration at the depth of 3 μm below the surface was reduced by a factor of 1% or 0.1%, therefore, the As-implanted doping layers of the samples were almost cleaned up after etching.

The energy gap E_g (unit: eV) of the films at all the experimental temperatures T can

be calculated from the formula in Refs.[5, 6]

$$E_g = -0.295 + 1.87x - 0.28x^2 + (6.0 - 14.0x + 3.0x^2)(10^{-4})T + 0.35x^4 ,$$

where x is the surface mole fraction of Cd in the films.

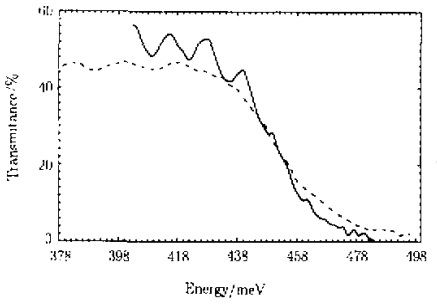

Fig. 1. The transmission spectra of sample 1 before and after etching. The sample was grown by MBE, implanted with As, and then annealed. The energy gap and the surface composition can be calculated by the method proposed in Refs.[2, 3, 4]. The film thickness is about 10 μm before etching and 7 μm after etching. Solid line: before etching; dashed line: after etching.

Figure 2 shows the photoluminescence spectra of sample 1 taken at several temperatures. The four photoluminescence peaks, which are labeled A, B, C and D, can be clearly observed.

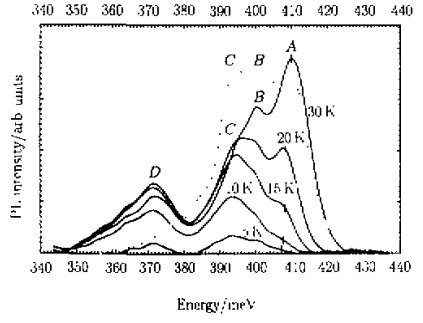

Fig. 2. The photoluminescence spectra of sample 1 at several temperatures before etching under the excitation by cw Ar^+ 514.5 nm laser beam with an output power of 300 mW (the exciting power density is 3 W·cm^{-2}). The dotted line refers to the 30 K photoluminescence spectra of sample 2 annealed at a temperature about 50°C lower than sample 1. (The composition nonuniformity has been corrected.) As for the other samples, annealed at lower temperatures, the photoluminescence cannot be observed. The dominant structures are labeled by A, B, C and D, the energy gap E_g for corresponding temperature is labeled with short bar.

Table 1. The Photoluminescence peak energy and the energy gap E_g of sample 1 at 30 K.

E_g/meV	The photoluminescence peak energy/meV			
	Peak A	Peak B	Peak C	Peak D
409.6	410	400	394	370

The dependence of photoluminescence peak intensity $I_{P.PL}$ on the exciting power P_I is shown in Fig.3(b), and it can be expressed as

$$I_{P.PL} = CP_I^{\nu} ,$$

where C is a constant and ν is a coefficient related to the recombination mechanisms. Schmidt *et al.*[7] have established an effective model to calculate the range of ν for various

kinds of recombinations in CdTe. Because $Hg_{1-x}Cd_xTe$ has a similar energy band structure to CdTe except for a narrower energy gap and a stronger band-to-band interaction, the same range of ν for $Hg_{1-x}Cd_xTe$ can be derived. That is

$$\nu_{\text{band to band}} > \nu_{BX} > \nu_{FX} > \nu_{\text{bound to free}} > \nu_{D^\circ A^\circ} ,$$

and just like CdTe, ν will have little changes depending on the concentration ratio of donor and acceptor N_D/N_A when the exciting laser power is varied over two decades except for the $D^\circ A^\circ$ transition where there is a tendency for ν to be saturated.

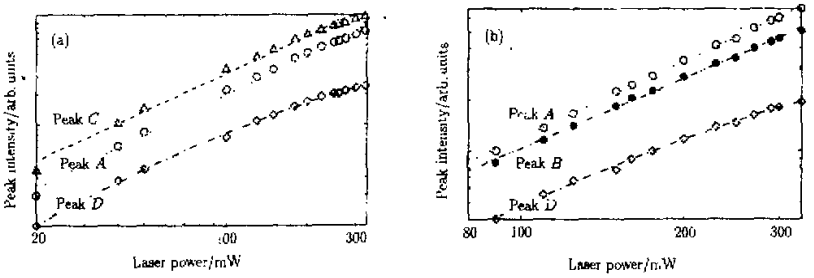

Fig. 3. The main photoluminescence peak intensity sample 1 vs. the power of the exciting laser. (a) 35 K after etching; (b) 30 K before etching. For the peak A, B and C, the slopes of the fitted line are represented by ν in formula $I_{P.PL} = CP_I^\nu$, and they are constants ranging from 1.0 to 2.0. For peak D, the saturation tendency of luminescence of $D^\circ A^\circ$ can be easily seen in (a) but not so obviously in (b), the explanation is given in the text. The lines between data points of peak D are drawn only for visual aid.

It is seen in Figs.2 and 3 that the energy of peak A is very close to E_g (less than E_g by only 1 meV). Its photoluminescence intensity is very weak at lower temperatures ($T < 20$ K) and becomes stronger at higher temperatures ($T > 30$ K). The coefficient ν of this peak is the largest among all the peaks and there is not any other peak on its upper energy side for all the experimental temperatures. Therefore peak A can be assigned for the band-to-band transitions. The photocurrent (PC) spectra of the multiple infrared detector line array made from this material lead to the same conclusion.

The rest three peaks can be analyzed on the basis of analyses of peak A.

Figure 4 shows the photoluminescence spectra of sample 1 whose doped layer was already removed by etching. It is easy to see that the peaks B and D are obviously weakened but the peak C is enhanced. The curves of $\log(I_{P.PL})$ vs. $\log(P_I)$ for samples before and after etching are shown in Fig.3. The peak A has no obvious change and it is still associated with the band-to-band transition. The peak C is at 16–17 meV less than peak A, its peak energy has the same temperature dependence as that of peak A and is not affected by the exciting power. Moreover, its coefficient ν is less than that of peak A. These experimental results suggest that peak C is due to the bound exciton (BX). The binding energy of exciton

is about 1.5 meV in $Hg_{1-x}Cd_xTe$ ($x \approx 0.39$). Thus the impurity level is 14.5–15.5 meV. In comparison with the Refs.[8–11], we know that it originates from Hg vacancies. In fact, it is impossible to avert the influence from Hg vacancies in $Hg_{1-x}Cd_xTe$.

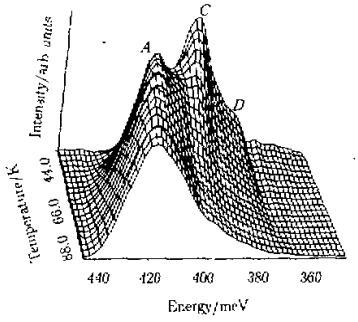

Fig. 4. The photoluminescence spectra of sample 1 (after etching) at several experimental temperatures.

The peaks B and D have not been reported as far as we know. Analyzing the dependence of peak energy and peak intensity on the exciting laser power and temperature, peak B is attributed to BX luminescence. However, it is exhibiting the characters in contrast with that of peak C which comes from the Hg vacancies bound excitons, peak B is strong before etching and it is almost too weak to recognize after etching, this fact just manifests that the peak B is related with the luminescence of bound exciton in the donor level formed from As-occupied mercury vacancies after annealing. This donor level is 8.5 meV.

Analysis of the peak D, however, is more complicated. The intensity of peak D is strong before etching and becomes weak after etching. It shows that peak D is related with As doping. The ν of peak D is not a constant and exhibits a saturation tendency as the exciting laser power increases. The blue shift of this peak was observed at lower excitation power. The peak intensity decreases rapidly with increasing temperature. Thus peak D is showing the typical characters of donor-acceptor (D^0A^0) pair. But in the case of Fig.3(b) where sample 1 was not etched, peak D did not thoroughly show those characteristics. The explanation is that the As ion concentration by implantation near surface is very high before etching so that the compensation of donor and acceptor is also very high. On the other hand, the exciting laser power was not very high in order to prevent the samples from surface damage. Although these reasons tend to conceal the true origin of peak D, the wide full-width at half-maximum (FWHM) of this peak still suggests that it is impurity-related. After etching, the concentration of As has 2 or 3 decades decrease and the compensation is lower, too. Thus the D^0A^0 transition characteristics of peak D can be easily observed.

In order to investigate the origin of peak D, another experiment was performed to make a comparison. The photoluminescence spectra of sample 2, which was annealed at 400°C, are also shown in Fig.2. There are three peaks, peaks A, B and C. The peak D can hardly be seen. These facts illustrated that peak D is not only related to As ion implantation, but also to annealing temperature. It is well known that the As-implanted $Hg_{1-x}Cd_xTe$ must be annealed at a temperature high enough for a long time to obtain the p-type layer formed by As-occupied Te site near the surface. Therefore, it can be inferred that peak D

is a luminescence peak of D^0A^0 pair at the acceptor level which is provided by As-occupied Te site. As for the donor level contributing to luminescence it is offered by the As-occupied mercury site, since only the peak related with the luminescence of bound exciton at As-occupied mercury site is obviously dominated in spectra. Thus, from the energy location of peak D and the 8.5 meV donor level coming from As in Hg site, we can infer that the acceptor level provided by As in anion site is about 31.5 meV in $Hg_{0.61}Cd_{0.39}Te$.

IV. CONCLUSION

A series of As-implanted $Hg_{1-x}Cd_xTe$ ($x \approx 0.39$) thin films which were annealed at different temperatures were investigated by means of photoluminescence spectroscopy. The band-to-band transition, bound exciton (BX) and D^0A^0 pair transition were observed in the experiments. By the aid of the dependence of photoluminescence peak energy and intensity on the experimental temperature and exciting laser power density, as well as by the comparison with the infrared transmission spectra, the origin of every peak was suggested. A donor level and an acceptor level, located at 8.5 meV below the bottom of the conduction band and 31.5 meV above the top of the valance band coming from the As in mercury site and As in anion site, respectively, are discovered experimentally.

ACKNOWLEDGMENTS

The authors wish to thank Li Biao, Liu Kun, Zhang Jia-ming and Jiang Shan for helpful discussion.

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