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Electron paramagnetic resonance study on annealing of phosphorus-implanted cadmium telluride

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This paper presents the investigations on the p-type conduction of the phosphorus-implanted CdTe single crystals. Previous theoretical calculations predicted the existence of large amounts of phosphorus interstitials in the as-implanted and thermally annealed samples and the elimination of these defects in the pulse electron-beam-annealed samples, which is confirmed in this work by the electron paramagnetic resonance measurements. This shows the significant effect of melting crystals in the pulse electron-beam annealing process on obtaining high carrier concentrations.

I. INTRODUCTION

Historically, p-type conduction with high carrier concentrations is not easily obtained for cadmium telluride (CdTe) single crystals. For example, Arkad’eva, Matveev, and Rud’4 prepared their CdTe single crystals by zone melting and converted them to p-type by simultaneous phosphorus introduction from the gaseous phase. The result showed a carrier concentration of about $10^{16}$ cm$^{-3}$. It was mainly due to the low solubility of dopants. Several works have been carried out to cope with this difficulty. Chu, Bube, and Gibbons5 utilized the ion implantation technique and thermally annealed their As$^{+}$ and P$^{+}$-implanted CdTe crystals. Uzan, Legros, and Marfaing3 used continuous-wave argon-ion laser to anneal P$^{+}$-implanted CdTe crystals. Both works showed hole concentrations in the order of $10^{17}$ cm$^{-3}$. In our laboratory4,5 a hole concentration as high as $5 \times 10^{16}$ cm$^{-3}$ was obtained in CdTe by P$^{+}$ implantation and pulse electron beam (PEB) annealing.

In a previous paper,6 a theoretical analysis was provided to explain the different effects of the different annealing processes. In this paper, the analysis is extended and further confirmed by including the experiment of electron paramagnetic resonances (EPR). Results show that it is the ability to eliminate the implantation-induced defects by melting crystals that makes the PEB annealing a favored process for annealing-implanted CdTe crystals.

II. EXPERIMENT

The CdTe single crystals were grown by the traveling heater method. After polishing and surface etching, phosphorus implantations were carried out at room temperature, at an incident energy of 100 keV and at various doses. PEB annealing was performed as described in Ref. 4. Some of the implanted samples were subjected to thermal annealing at 300–400 °C for about 1 day.

EPR measurements were performed at room temperature using a Bruker 200D 10/12 system with the microwave frequency in the X band. A sample holder was designed so as to allow the rotation of samples. Four kinds of samples (as-grown, P$^{+}$ implanted, P$^{+}$ implanted and thermally annealed, as well as P$^{+}$ implanted and PEB annealed) were subjected to the EPR measurements.

III. RESULTS

No EPR signals were detected for the as-grown and E-beam annealed samples. For the other two kinds of samples, similar spectra were obtained. Figure 1 shows the typical ones. With the magnetic field in the (110) plane, an isotropic signal was detected with the $g$ value ranging only slightly around 2.20. The linewidth is about 125 G. The signal is accompanied with the vague satellites.

It has been uneasy to detect EPR signals for undoped CdTe crystals.7–9 Even at 4 K only a very small signal has been reported.7 This may be due to that most of the defects in undoped CdTe crystals are not paramagnetic and/or to that paramagnetic centers are of low concentrations or short living.

From Fig. 1, the lack of clear hyperfine interaction signals indicates that the unpaired electron is not located near phosphorus (100% natural abundance of $I = 1/2$ atoms) and cadmium (25% natural abundance of $I = 1/2$ isotopes), but rather at tellurium (8% natural abundance of $I = 1/2$ isotopes). The shift of the $g$ value in CdTe has been discussed in Ref. 9 and our observed positive $g$ shift coincides with the involvement of Te atoms. The broad linewidth shows the interactions of the electron with the surrounding atoms. By the self-consistent field calculation of the atomic structures, the quantity $(r_i^2)$ for the 5p orbitals of Te atoms was estimated to be about $95 \times 10^{-24}$ cm$^{-3}$ which corresponds to the separation between the symmetric satellites. Along with the vagueness of the satellites, which coincides with the small abundance of $I = 1/2$ Te isotopes, we conclude that the EPR signal comes from the electrons near Te atoms.

IV. DISCUSSION

In this work, the prediction about the existence of the EPR signals at various stages had been made before the experiment, which is shown as follows: During implantation, damages are produced in the target crystals. These implantation-induced defects may play important roles in the conduction of carriers. A procedure estimating the types and quantities of them has been developed and the details were described in Ref. 6. It was noted that the number of implanted atoms is about three orders higher than those of displaced...
Either laser or electron pulses can be used for transient annealing. The beams couple energies to the targets by different mechanisms but they produce ultimately the same effect—heat—for annealing samples. The samples may or may not be melted to certain depths under different experimental conditions, and it is expected that the melting of the targets plays an important role in eliminating the implantation-induced damages. In the cases in Ref. 3, samples were not melted. But in our experiments, the surfaces of CdTe crystals were melted to depths of several micrometers. Thus phosphorus atoms diffuse easily and redistribute during the melting-recrystallizing process. The redistribution profiles of dopants have been obtained and Fig. 2 shows the results. It is noted that the profiles of phosphorus atoms match those of holes quite well, which indicates that phosphorus atoms play major roles in the p-type conduction after the PEB annealing. It was reasoned that the pulse electron beam quickly melts the samples to certain depths, which removes the obstacles for the dopants to occupy the lattice sites. Because of their sizes and electronegativities, it is easier for phosphorus atoms to occupy Te sites than to occupy Cd sites when recrystallizing, which thus may give high hole concentrations. In addition, almost all the $P_{Te}$ acceptors are ionized at room temperature and they should give no EPR signals.

All these reasonings are confirmed by our EPR measurements. From the above investigations, a logical model about the atom arrangements in CdTe during the phosphorus implantation and the annealing processes have been obtained which could be an explanation of the p-type conduction.

![First derivative of absorption (a.u.)](image1)

**FIG. 1.** EPR spectra of CdTe single crystals. (a) Phosphorus implanted; (b) phosphorus implanted and thermally annealed.

There are two types of interstices in CdTe single crystals: one is surrounded by Cd atoms and the other by Te atoms. By the electronegativity considerations, most phosphorus interstitials are of the former type and are expected to be more thermally stable than the other type. In this atom arrangement, because of the larger electronegativity of phosphorus atoms, they would break the nearest Cd-Te bonds and construct the bondings between them and the nearest Cd atoms, thus leaving dangling bonds near tellurium atoms which should give rise to EPR signals. Besides, the expected thermal stability of these phosphorus interstitials should lead to the observation of the same EPR signals in the thermally annealed CdTe samples as in the as-implanted ones.

![First derivative of absorption (a.u.)](image2)

**FIG. 2.** Profiles of holes (solid lines) and redistributed phosphorus atoms (dashed lines). (a) PEB annealed, dose = $5 \times 10^{15} \text{ cm}^{-2}$; (b) PEB annealed, dose = $4.62 \times 10^{14} \text{ cm}^{-2}$; (c) thermally annealed as obtained by Chu et al. in Ref. 2.
duction data. Although one cannot conclude without further consideration that the phosphorus atoms occupy the Te sites after the PEB annealing to give holes, confidence in this reasoning can be gained from the electronegativity consideration, the good match between the hole profiles, the phosphorus redistribution profiles after the PEB annealing, and the correspondence between the prediction on the EPR signals and the experimental results.

The merit of the ion implantation technique is to overcome the problem of the limited solubility in CdTe. However, most implanted phosphorus atoms stay in thermally stable interstitial sites which cannot be easily removed by the thermal annealing process. It is the melting effect of the PEB annealing technique that removed these defects and opened the door for phosphorus atoms to occupy the Te lattice sites.

If the samples were not melted, the phosphorus interstitials could not be efficiently eliminated even though pulse energy beams were employed. This can be reasonable by referring Ref. 3 in which pulse laser beams were used but samples were not melted. EPR investigations on these samples should provide more understanding. Besides, the thermal stability of the phosphorus interstitials is still not justified. Theoretical studies on this subject deserve to be undertaken.

As an interesting point, forming amorphous layers in CdTe by implanting high-dose, high-energy arsenic ions could facilitate the thermal annealing technique in eliminating defects to obtain high hole concentrations, which is an easier technique and is more suitable for mass production. To test this idea, a CdTe single crystal was As+ implanted ($E = 130$ keV, dose = $1 \times 10^{16}$ cm$^{-2}$) and thermally annealed, and the EPR measurements were done before and after annealing. Before the annealing, the same EPR signal as that in P+ implanted samples was observed. But after the annealing, this signal disappeared. This could be a first approval to the idea. Further investigations are required.

V. CONCLUSION

Better understanding in obtaining good p-type conduction in CdTe single crystals has been achieved by theoretical calculations$^6$ for several processes and the EPR experiment. Good matches between the theoretical predictions and the experimental results confirm our model. High hole concentration was achieved in CdTe by using phosphorus implantation and PEB annealing techniques, and the melting effect of PEB annealing is a determining factor for the resultant electrical properties.

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