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Identification and Investigation of Impurities in Undoped $Hg_{1-x}Cd_xTe$

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The effect of impurities on electrical properties has been the most sought information for the well-known infrared sensing material mercury–cadmium telluride. The relationship between the excess holes (p-type) or excess electrons (n-type) of undoped mercury-cadmium telluride $Hg_{1-x}Cd_xTe$ ($0.23 \simeq x \simeq 0.4$) and the residual impurities in the crystals were investigated. The impurities in the undoped material were determined using emission spectrometry, atomic absorption, and spark sources mass spectrometry.

Trace analysis indicates that impurities such as Cu and Ag consistently appear in p-type samples. Although these elements are not frequently observed in n-type substance, occasionally they are found in the material in a minute amount. Impurities such as Si, Cr, Pb, Li, Rb, Co, and Sn have been detected in both p-type and n-type materials. The possible correlation of these impurities with the p-type or n-type behavior of the undoped material is discussed.

Introduction

Mercury–cadmium telluride (Hg, Cd)Te has a general formula $Hg_{1-x}Cd_xTe$. When the value of x is higher than 0.15 the material is an intrinsic semiconductor that can be used in high performance infrared detectors operating at a relatively elevated temperature (*1*). The continuous variation of the energy gap with composition x allows us to design for optimum performance of the $Hg_{1-x}Cd_xTe$ detectors at wavelengths between about 1 and 14 μm. This material is now adequate for many ir detector applications. However, this alloy system will not achieve full potential unless it is produced with near-intrinsic carrier concentrations. With $x = 0.2$, for instance, the material has approximately 3×10^{22} atoms cm^{-3} and a band gap of about 0.1 eV with a typical carrier concentration in the range of 10^{15} cm^{-3} at 77°K. The intrinsic carrier concentration of the material is estimated to be about 10^{13} cm^{-3} under similar conditions (*2*). Observations show that this excess of carriers has not been significantly changed by a careful annealing treatment (*3*). This suggests that impurities in the bulk material may provide the excess carriers. Identification of impurities and investigation of their effects on electrical properties should allow efficient application of (Hg, Cd)Te in infrared detection and should be beneficial to future researches in this area. Primarily, our approach was to select a large number of (Hg, Cd)Te samples having either excess holes (p-type) or excess electrons (n-type) to study and compare their impurity contents. Establishment of a correlation between the electrical measurement and the chemical analysis was our ultimate goal. Crystals doped with known impurities were prepared to confirm the observed electrical effects. Preliminary trace impurity investigations were performed using emission spectrometry (*4*), atomic absorption (*5*), and spark source mass spectrometry (*6, 7*).

This paper describes the validity of these

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analytical methods in trace analysis for identifying the impurities present in the undoped (Hg, Cd)Te crystals and to study the effects of these impurities upon the electrical properties of the ir sensing material.

Experimental

Materials

Mercury was obtained from Hg^n Inc., Milwaukee, Wisconsin. Cadmium and tellurium were obtained from Cominco American Inc., Spokane, Washington. Te was purified by zone refining; Hg and Cd were used as received. The purities of all starting materials were checked by emission spectrometry and variations of purities were observed from lot to lot of samples. Typical results of the analysis are summarized in Table I.

The (Hg, Cd)Te samples were prepared by loading a stoichiometric composition of Hg, Cd, and Te into a sealed quartz ampoule which was heated to 900°C and then was rocked to ensure mixing. The cooling process was programmed from tip to tail and yielded a dendritic crystalline form. This preliminary material was converted to a microscopically homogeneous material by annealing. The type of conductivity and the carrier concentration were determined by thermoelectric probing and Hall effect measurement.

Emission Spectrometry

The emission analysis was accomplished with the Baird three-meter spectrograph.

TABLE I

TYPICAL IMPURITIES IN THE STARTING MATERIAL FOR GROWING (Hg, Cd)Te CRYSTALS AS DETERMINED BY EMISSION SPECTROSCOPY

Impurity concentration (ppm)	Hg	Cd	Te
10–1	None	None	Mg, Si
1–0.1	None	Cu	Cu, Ag, Fe
Trace	None	Ag, Pb Fe, Mg Si	Sn

In general, a sample was placed in a high-purity graphite-cupped electrode. The common electrode pair employed in the study consisted of cathode ultra 5710 and Anode ultra 7423. The analytical gap was 3 mm using a low voltage dc arc burning for 75 sec at 13 A. In some instances, a step-burning technique was used to obtain a maximum sensitivity and resolution. The step-burning was performed in sequence at 5, 10, and 11 A with 60 sec for each step. The slit width and length were 20 μm and 2.5 mm, respectively.

The sensitivity of the measurement was determined by preparing (Hg, Cd)Te samples of known impurity concentrations using mixtures of (Hg, Cd)Te and Spex mix (Spex Industries Inc., Metuchen, New Jersey). Spex mix is a high purity graphite homogenized with the oxides of 49 elements, such as Ag, Al, As, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, F, Fe, Ga, Ge, Hg, I, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Sb, Se, Si, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Zn, and Zr. The (Hg, Cd)Te samples were prepared with five different impurity levels: 0.5, 1.0, 2.5, 5.0, and 10 ppm by weight. A sample was arced to determine the limit of detection, which was then used to estimate the range of impurities in the unknown.

For high accuracy measurements, a standard method of addition can be applied (*8*). In this method, the unknown is used as the base material. An appropriate quantity of the element under consideration is added to the unknown. Several standards can be prepared while one is retained with no additions. The intensity ratio of the analysis line (of the element of interest) and the Cd (2929 Å) line (an internal standard) is plotted against the concentration of the element added. If the intensity ratio from an unknown base sample (which has nothing added) and that from the added samples changes linearly with the amount of the addition, the concentration of the element in the unknown can be evaluated from the intercept at the abscissa of the plot. This addition method is illustrated in Fig. 1 for the case of Ag addition in undoped (Hg, Cd)Te. The result of this example indicates that the Ag content in the sample is 0.2 ppm.

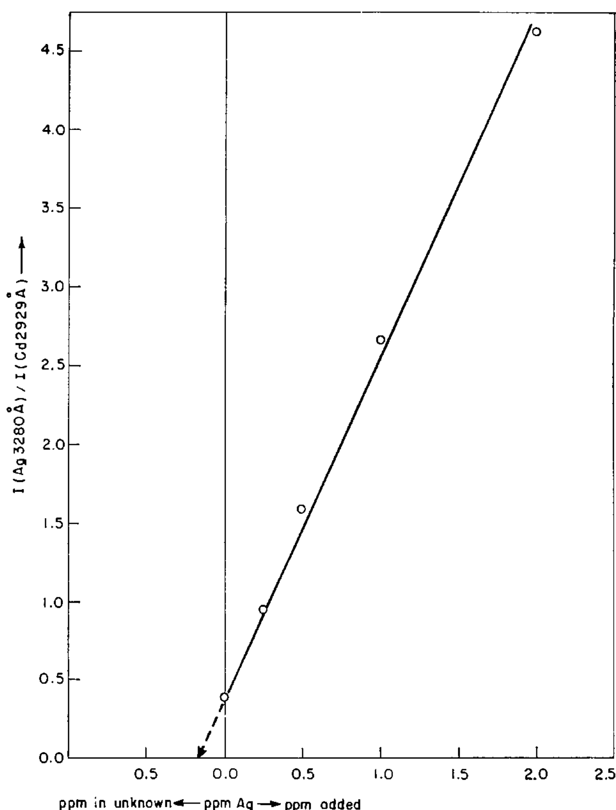

FIG. 1. Determination of Ag content in (Hg, Cd)Te by method of standard additions using emission spectrometry.

Atomic Absorption

Atomic absorption analysis of trace impurities were determined on a Varian Techtron model AA-5R. A sample of approximately 250 mg was dissolved in 5–10 ml of 1:2 HCl:HNO_3. The solution was diluted to a final volume of 25 ml with deionized water. Three aliquots of the sample were taken from the solution for measurements. Also, the standard method of addition (*8*) was employed. Additions containing 0.025 and 0.05 $\mu g\ ml^{-1}$ of the elements were made to two of the aliquot samples. The third sample was retained as a standard. The measured absorbance was plotted versus the concentration of the added element. The resulting linear plot was extrapolated to zero absorbance. The intercept on the concentration axis gave the concentration of the impurity in the diluted sample. Then, the impurity concentration in the solid (Hg, Cd)Te could be calculated. The determination of Ag content in (Hg, Cd)Te by atomic absorption techniques is illustrated in Fig. 2.

Spark Source Mass Spectrometry

A spark source mass spectrometer, CEC 21-110B, was used to determine impurities in (Hg, Cd)Te. The samples were two bars 10 mm long by 1.5 mm square. The bars were mounted in the ion source with their tips separated by approximately 1.5 mm. The source chamber was evacuated and a spark was initiated between the bars by applying a pulsed RF voltage. Positive ions representative of the composition of the samples were formed within the ion source. A mass spectrum was recorded on a photographic plate. Impurity concentrations were estimated by comparing the intensity obtained from a

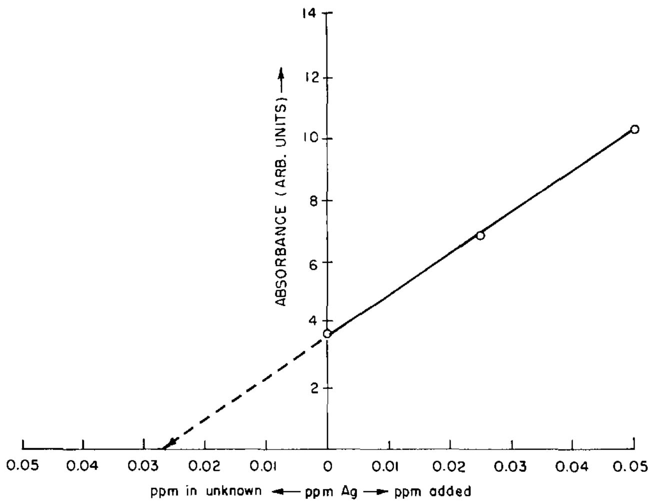

FIG. 2. Determination of Ag content in Ag doped (Hg, Cd)Te by method of standard additions using atomic absorption spectrophotometry. The concentrations shown are those of the diluted sample solutions.

sample to that of the internal standard Hg^{3+}_{196}.

Results and Discussion

Table I shows the impurities found in the materials for growing (Hg, Cd)Te as identified by emission spectrometry. Some impurities might have been overlooked due to their low sensitivity to the measurements. These results indicate that the purity content of the Hg is very low and the material is satisfactory for crystal growth. The finding also has excluded a potential source of contamination.

Cu was occasionally detected up to a few ppm and Ag, Pb, Fe, Mg, and Si frequently appear at a fraction of a ppm in Cd. Mg, Si, Cu, Ag, Fe, and Sn consistently appeared in double zone refined Te ranging from a fraction of a ppm to a few ppm. The relation of the purity in the starting Cd to the final (Hg, Cd)Te crystals has not been determined. It is difficult to specify a further purification. It is obvious that a higher purity of Te is most desirable. Double zone refining appeared to be not successful in removing all the impurities and a further purification technique is needed.

Table II presents the minimum detectable impurities in 100 mg of (Hg, Cd)Te samples as detected by emission spectrometry using the step-burning techniques. The lowest limit of detection is defined as a concentration that produces a spectral line of 5% transmittance above the background. A good sensitivity down to 0.5 ppm or lower for Cu, Ag, Be, Mg, Mn, B, Bi, Ni, Co, V, Mo, and Si in the (Hg, Cd)Te matrix was achieved using the present technique. Elements such as Sn, Al, Pb, Ga, Ge, and In could be detected easily at a concentration of 1.0 ppm. Ti, Fe, and Sb could be measured at

TABLE II

DETECTION LIMITS OF IMPURITIES PRESENT IN (Hg, Cd)Te MATRIX AS MEASURED BY EMISSION SPECTROMETRY

Minimum detectable impurities (ppm)	Impurities in (Hg, Cd)Te matrix
0.5 and lower	Cu, Ag, Be, Mg, Mn, B, Bi, Ni, Co, V, Mo, Si
1.0	Sn, Al, Pb, Ga, Ge, In
2.5	Ti, Fe, Sb
5.0	Cr, Zr
10 and above	Na, Zn, Ca, P, Nb, Ba, etc.

2.5 ppm. Impurities such as Cr and Zr required 5.0 ppm to provide good detections. Finally, the remaining elements needed a concentration of 10 ppm or higher for observations. This means that the sensitivity of detection by this method depends greatly on the elements in the matrix system. This limits the analytical method to those impurities with high sensitivities. However, the linear relationship between the intensity ratio and the standard addition of impurity, as shown in Fig. 1, is clearly displayed. This observation assures the accuracy of the method in determining an impurity in such a complicated matrix. Similarly, Fig. 2 presents the linear relationship between the absorbance and an addition using atomic absorption spectrophotometry. These two techniques have been satisfactory in determining Cu and Ag impurities and will be discussed later in this paper. The methods also have given consistent results in determining In and Al in the (Hg, Cd)Te.

Table III shows trace impurities in *p*-type and *n*-type undoped (Hg, Cd)Te samples using emission spectrometry and atomic absorption. The results are obtained from about 20 samples of each type. Cu, Ag, and Si were the three impurities that consistently appeared in *p*-type samples at a concentration range of 0.13–0.61, 0.39–0.77, and 0.8–1.5 ppm, respectively. Other impurities, such as Sn and Pb, were observed only occasionally. Si was the only impurity consistently detected in *n*-type samples. Cu and Ag were not observed in the great majority of *n*-type samples except for two runs.

TABLE III

DETERMINATION OF TRACE IMPURITIES IN *p*-TYPE AND *n*-TYPE (Hg, Cd)Te BY EMISSION SPECTROMETRY AND ATOMIC ABSORPTION

Impurity	Concentration (ppm) *p*-type	Concentration (ppm) *n*-type	Weight of impurity barely detectable (ppm)
Cu	0.13–0.61	0.1–<0.05	0.05
Ag	0.39–0.77	0.1–<0.05	0.05
Pb	1.2 –1.0	1.0	1.0
Si	0.8 –1.5	0.8–1.5	0.5
Sn	1.3 –1.0	1.0	1.0

Table IV summarizes the results of trace analysis on (Hg, Cd)Te using the spark source mass spectrometry. However, the mass spectra of (Hg, Cd)Te samples were difficult to interpret because multiple-charged ions from the (Hg, Cd)Te matrix tended to mask trace impurities. Impurities such as Fe, Mn, Ni, and Cu were subjected to direct matrix interference from Cd and Te and yielded no useful information. Significant signals were observed from the elements Si, Ag, Cr, Pb, Li, Rb, and Co. Among them Li, Rb, and Co are impurities present at low trace levels. Si, Cr, Ag, and Pb are found at approximate concentrations from a fraction of ppm to several ppm. All of these impurities were commonly observed in both *p*-type and *n*-type specimens, except Ag which was consistently observed only in *p*-type samples.

TABLE IV

SUMMARY OF SPARK SOURCE MASS SPECTROMETRY DETERMINATION OF IMPURITIES IN *p*-TYPE AND *n*-TYPE (Hg, Cd)Te

Concentration	(Hg, Cd)Te specimen *p*-type	(Hg, Cd)Te specimen *n*-type	Remarks
1 ppm and above	Si	Si	No information for Fe, Mn, Ni or Cu due to direct matrix interferences
0.1–1 ppm	Ag, Cr, Pb	Cr, Pb	
Trace	Li, Rb, Co	Li, Rb, Co	

TABLE V

CORRELATION OF ANALYTICAL RESULTS AND ELECTRICAL MEASUREMENTS

Dopant	*HCT* Sample	Impurity found (ppm)	Impurity found (atom cm^{-3})	Impurity added (atom cm^{-3})	Electrical (n)[a]
Cu	31574*M*-2	1.9	1.1×10^{17}	1.0×10^{17}	0.9×10^{17}
Cu	31574*Q*-2	1.2	0.7×10^{17}	1.0×10^{17}	0.9×10^{17}
Cu	31574*Q*-8	2.8	1.6×10^{17}	1.0×10^{17}	0.9×10^{17}
Ag	31974*L*-1	2.2	0.8×10^{17}	1.0×10^{17}	1.1×10^{17}
Ag	31974*T*-1	2.8	0.9×10^{17}	1.0×10^{17}	1.1×10^{17}

[a] 77°K carrier concentration determined by Hall effect measurements.

Agreement on the Ag impurity among these three analytical methods is very good.

Comparison of the impurities identified in the *p*-type and *n*-type (Hg, Cd)Te samples indicates that impurities such as Cu and Ag consistently appeared in the *p*-type specimens and were not often observed in *n*-types; although occasionally they were identified at significantly low concentrations. Cu and Ag may well become electron acceptors since they are in the *IB* group and are probably located in the Hg or Cd lattice sites. In other words, the remaining Cu and/or Ag impurities seem to play a significant role in generating the excess holes in the *p*-type undoped (Hg, Cd)Te. However, results of impurity analysis using these three analytical methods give no clue whatsoever of which impurity or impurities are the cause of excess electrons in the *n*-type undoped (Hg, Cd)Te.

To confirm the *p*-type effects of Cu and Ag impurities in the (Hg, Cd)Te, two (Hg, Cd)Te ingots were doped separately with Cu and Ag at a nominal concentration of 10^{17} atom cm^{-3}. The carrier concentrations were determined by Hall measurements. The Cu or Ag concentrations of the same sample were determined by atomic absorption. The results of these tests are summarized in Table V, which shows that the Cu and Ag determinations closely match the added quantities and are approximately equal to the acceptor concentration. These results suggest that the remaining Cu and Ag must be the major hole contributors of the undoped (Hg, Cd)Te.

It is evident that Te, and probably Cd, are the major sources of contamination. Other sources include the deionized water used for cleaning, the quartz reaction ampoule, the CH_3OH/Br solution used for etching, and substances encountered during handling. Further identification of the origin of impurities and improved methods for their prevention are underway. The results will be released at some appropriate future time.

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